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The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W. 1.

CXXXIV.—*Studies in the Fenchene Series. Part I. A Synthesis of* apo*Fenchocamphoric Acid.*

By WALLACE FRANK SHORT.

APART from the syntheses of *l*-β- and *d*-α-fenchene from nopinolacetic acid by Wallach (*Annalen*, 1907, **357**, 82; 1908, **363**, 1) and of *r*-fenchone by Ruzicka (*Ber.*, 1917, **50**, 1362), a *complete* synthesis has not yet been effected in the fenchene series. In order to achieve this, a favourable starting-point would appear to be *apo*fenchocamphoric acid. Hitherto this acid has been obtained from camphenilane by oxidation with nitric acid (Nametkin and Chuchrikovaia, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 425; Nametkin and Michailovna, *ibid.*, 1917, **49**, 417) and, in almost theoretical yield, from β-fenchocamphorone by oxidation with potassium permanganate (Komppa and Roschiev, *Ann. Acad. Sci. Fennicae*, 1917, *A*, **15**, 1; Roschiev, *ibid.*, 1919, *A*, **10**, 1; Komppa and Roschiev, *Annalen*, 1922, **429**, 175; Nametkin, *ibid.*, 1924, **438**, 185). It is regarded as 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid; this structure, however, has not been definitely established (compare Roberts, *J. Amer. Chem. Soc.*, 1926, **48**, 1975). The acid has now been synthesised by the condensation of *iso*butylene dibromide with ethyl disodiopropane-αα*γγ*-tetracarboxylate according to the classical methods of the Perkin school. The yield is very small owing to loss of bromine from the *iso*butylene dibromide with formation of *iso*butylene, α-bromo*iso*butylene, and other compounds, and is, moreover, adversely affected by slight variations in the conditions of preparation. Loss of hydrogen bromide was anticipated from the observations of other investigators (Bentley, J., 1895, **67**, 266), but the loss of both bromine atoms was somewhat unexpected, since Otto and Mühle (*J. pr. Chem.*, 1895, **51**, 519) state that *iso*butylene dibromide is attacked by sodium only with difficulty.

Although the synthesis is uneconomical, it establishes the constitution of *apo*fenchocamphoric acid as 4 : 4-dimethyl*cyclo*pentane-1 : 3-dicarboxylic acid.

EXPERIMENTAL.

Ethyl propane-αα*γγ*-tetracarboxylate (b. p. 194—195°/11 mm.) (88·5 g.; 1 mol.) and 130 c.c. of toluene were shaken with 9·2 g. (1½ atoms) of powdered sodium until this dissolved; 43·2 g. (¾ mol.) of *iso*butylene dibromide (b.p. 36—37°/10 mm.; Taboury, *Bull. Soc. chim.*, 1911, **9**, 125) were then added and the mixture was boiled for 60 hours. *iso*Butylene was steadily evolved and sodium

bromide deposited. The product was poured into water and the oil so obtained was distilled under 10 mm. pressure. After removal of the substances boiling below 194°, there remained a small quantity of a thick syrup. This was boiled for 3 hours with 3 g. of potassium hydroxide dissolved in alcohol. The acid obtained on acidification, m. p. 170—179° (decomp.), was heated at 220—230° until the evolution of carbon dioxide had ceased. The semi-solid residue was washed twice with 10 c.c. of water, which extracted a small quantity of glutaric acid. The dried residue, m. p. 110—115°, was treated with 6 g. of acetyl chloride for 2 days, the excess of the latter then removed at 60° under reduced pressure, and the residue was shaken with 11 c.c. of cold 5% caustic soda solution, washed with water, dried, and recrystallised from benzene–light petroleum. It melted at 136—137°, and by solution in hot 10% caustic soda solution and reprecipitation with sulphuric acid, 0·6 g. of an acid (m. p. 143—145°) was obtained (*cis-apo*fenchocamphoric acid melts at 144·5—145°). From the acidified 5% caustic soda extract, crystals (1·3 g.) were deposited which melted at 147—148° after recrystallisation from ether (Found: C, 58·2; H, 7·6 by the micro-Pregl method; equiv., 93·6. Calc. for $C_9H_{14}O_4$: C, 58·1; H, 7·5%; equiv., 93·0). *trans-apo*Fenchocamphoric acid melts at 147—148° (Nametkin, *Annalen*, 1924, **438**, 185). The total yield of *apo*fenchocamphoric acid was 1·9 g. or 5% of the theoretical.

The author is indebted to the Chemical Society for a grant which partly defrayed the cost of this research, and to Prof. J. K. H. Inglis for an arrangement which prevented overlapping.

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NEW ZEALAND. [*Received, December 7th*, 1926.]

CXXXV.—*The Action of Nitric Acid on Acetylene and Ethylene.*

By PHYLLIS VIOLET MCKIE.

IT has been shown (Orton and McKie, J., 1920, **117**, 283) that the principal products of the interaction of fuming nitric acid with acetylene are carbon dioxide and trinitromethane. In the reaction between fuming nitric acid and ethylene a similar formation occurs, but prior to the production of trinitromethane the addition compound, β-nitroethyl alcohol, is formed.

It is now possible to formulate a course of reaction between nitric acid and an ethylenic or acetylenic compound. From the presence in the products of (*a*) β-nitroethyl alcohol (from ethylene)

and (*b*) nitrolic acids, and the direct formation of nitroparaffins from these compounds, it is deduced that the primary reaction is one of addition of hydroxyl and the nitro-group to the unsaturated linking, forming the nitro-alcohol. This, in the case of acetylene, becomes by further addition the unstable dinitrodihydroxy-compound. Oxidation and reaction with nitrous acid gives the corresponding nitrolic acid, together with carbon dioxide, from which trinitromethane is finally derived. Such a reaction is entirely in harmony with the reaction between oxides of nitrogen and unsaturated linkings (Schmidt, *Ber.*, 1901, **34**, 3536; 1902, **35**, 2323) and with the addition of nitric acid to various unsaturated compounds (Wieland and Rahn, *Ber.*, 1921, **54**, 1770; Cohn, *Ber.*, 1891, **24**, 3865).

The following equations represent the probable courses of reaction :

Acetylene : $CH{:}CH \longrightarrow CH(OH){:}CH(NO_2) \longrightarrow [CH(OH)_2{\cdot}CH(NO_2)_2] \longrightarrow CH(NO_2)_2{\cdot}CHO \longrightarrow CH(NO_2)_2{\cdot}CO_2H \longrightarrow CH_2(NO_2)_2 + CO_2$

$CH_2(NO_2)_2 \longrightarrow C(NO_2)_2{:}N{\cdot}OH \longrightarrow CH(NO_2)_3$

Ethylene : $CH_2{:}CH_2 \longrightarrow CH_2(OH){\cdot}CH_2(NO_2) \longrightarrow CH_2(NO_2){\cdot}CHO \longrightarrow CH_2(NO_2){\cdot}CO_2H \longrightarrow CH_3{\cdot}NO_2 \longrightarrow CH(NO_2){:}N{\cdot}OH \longrightarrow CH_2(NO_2)_2 \longrightarrow C(NO_2)_2{:}NOH \longrightarrow CH(NO_2)_3$.

Experimental.

Dry ethylene (97—99% purity), prepared by the vaporisation of ethyl alcohol in an iron combustion tube packed with pumice stone soaked in syrupy phosphoric acid and heated to 250—300°, was passed into fuming nitric acid diluted to various concentrations. The experimental procedure was in all respects similar to that used for acetylene (Orton and McKie, *loc. cit.*). The absorption of ethylene by concentrated nitric acid is rather less ready than is that of acetylene, and there is a markedly lower evolution of carbon dioxide. The ratio Carbon dioxide evolved/Ethylene absorbed is, for 95% nitric acid, 0·4 : 1; whereas the ratio Carbon dioxide evolved/Acetylene absorbed is 0·8 : 1; in the presence of mercury salts, however, these ratios show a closer approximation. The yield of tetranitromethane obtained by further nitration of the product (Orton and McKie, *loc. cit.*), expressed as a percentage of the hydrocarbon absorbed, in the ethylene reaction never rises to, and is often much less than, the value obtained for acetylene, and no variation of experimental conditions has altered this relation. The maximum yield of tetranitromethane in one operation in the absence of a catalyst is obtained by the absorption of 2·7—2·9 l. of acetylene or of 2·9—3·1 l. of ethylene by 100 g. of 95% nitric acid. The yield of tetranitromethane is 9—10 g. (from acetylene),

or 277% of the acetylene absorbed, or 6—7 g. (from ethylene), or 231%. The addition of 0·66% of mercuric nitrate raises the value for ethylene to 332·9% (compare acetylene, 453—532%). Hence the amount of carbon in the ethylene reaction used up in side reactions is considerable, 30—40%, which can partly be accounted for by the formation of oxalic acid representing 28%.

TABLE I.

% HNO_3.	Per 100 g. of HNO_3. C_2H_4 (l.) absorbed.	Per 100 g. of HNO_3. CO_2 (l.) evolved.	$C(NO_2)_4$ as percentage of C_2H_4 absorbed.	% C in C_2H_4 becoming $C(NO_2)_4$.	% C in C_2H_4 becoming CO_2.	% C in C_2H_4 becoming other substances.
100	2·146	—	98·4			
97·5	3·100	—	116·2			
95·0	2·980	—	231·8			
95·0	2·764	2·504	204·3			
90·0	2·980	0·210	198·1			
90·0	2·846	0·451	201·4			
Compare acetylene :						
95·0	2·288	2·855	278·7			
0·33% Mercuric nitrate as catalyst.						
95·0	2·900	1·930	300·4	21·46	37·98	40·56
0·66% Mercuric nitrate as catalyst.						
95·0	3·044	2·453	332·9	23·78	40·3	35·92
Compare acetylene :						
95·0	3·02	4·39	383·0	29·2	70·8	0·0

TABLE II.

Relation between oxalic acid produced and hydrocarbon absorbed.

% HNO_3.	Hydrocarbon absorbed (l.).	CO_2 evolved (l.).	$H_2C_2O_4$ (g.).	$\frac{CO_2}{H_2C_2O_4}$ by wt.	% C becoming CO_2.	% C becoming $C(NO_2)_4$.	% C becoming $H_2C_2O_4$.	Carbon unaccounted for.
Ethylene :								
95	3·152	2·699	2·774	1·93	42·5	25·34	21·61	10·55
90	1·484	0·608	1·710	0·71	20·49	29·8	28·34	21·37
Acetylene :								
95	3·792	3·212	2·357	2·69	42·15	17·42	15·29	25·14

Influence of Mercuric Nitrate.—Mercuric nitrate has, as in the reaction with acetylene, a favourable effect on the rate of absorption of ethylene and hence on the speed of interaction, and considerably increases the yield of nitroform. The effect of the mercury salt is complex, but is largely to prevent the alternative reaction of simple oxidation, thus increasing proportionally the addition reaction producing the nitro-alcohol. Side reactions are considerably reduced in its presence. A higher concentration of mercuric nitrate

was required to produce the maximum absorption of ethylene and the maximum yield of tetranitromethane than in the case of acetylene, and 0·66% was found to promote the best results. The ratio of Carbon dioxide evolved/Ethylene absorbed approached unity under the optimum conditions, but exceeded it only in exceptional cases.

Isolation of β-Nitroethyl Alcohol.—The product of the reaction between ethylene and fuming nitric acid was diluted with water, neutralised with sodium carbonate, and extracted with ether. From the washed and dried extract, by fractional distillation under diminished pressure, β-nitroethyl alcohol was obtained as a faintly yellow oil, b. p. 117—121°/30—35 mm.

The amount of nitroform which can be extracted and estimated by the ordinary procedure is always in excess of the alcohol, the ratio of alcohol to nitroform being approximately 1 : 2·4. The presence of mercuric nitrate seems to have little effect on this ratio. If, however, the estimation of the two compounds be carried out before the completion of the reaction, this ratio is markedly different; the amount of nitroform which can be isolated at such stages is appreciably less than that at the end of the reaction, whereas the amount of nitro-alcohol is not. The ratio of the two substances when half the normal quantity of ethylene had been passed was unity. Two facts of importance emerge from these data. Nitroform is produced subsequently to and, it would appear, at the expense of the nitro-alcohol, and the formation of nitroform takes place largely towards the end of the passage of the hydrocarbon.

TABLE III.

Relation between β-nitroethyl alcohol and nitroform.

Experiment.	β-Nitroethyl alcohol (g.).	Nitroform (g.).	Nitro-alcohol / Nitroform
95% HNO_3. No Hg	1·98	4·6	1 : 2·32
95% HNO_3. Hg	4·59	11·4	1 : 2·48
95% HNO_3. No Hg (½ ethylene passed)	1·36	1·9	1 : 1·4
95% HNO_3. Hg	3·38	5·14	1 : 1·52

The author is indebted to the Chemical Society for a grant which partly defrayed the cost of this work.

BEDFORD COLLEGE, LONDON. [*Received, February 15th*, 1927.]

CXXXVI.—*The Production of Fog in the Neutralisation of Alkali with Hydrogen Halides.*

By Henry Oscar Askew.

When a current of air carrying phosgene (carbonyl chloride) is passed through charcoal and then bubbled through an aqueous-alcoholic solution of sodium hydroxide, a fog appears in the flask containing the alkali as soon as the charcoal is saturated with phosgene. This fog persists even when the air in which it is suspended is passed through another similar absorption vessel.* If the phosgene is replaced by phosphorus oxychloride, similar observations are made.

A preliminary investigation of this phenomenon soon showed that neither the phosgene nor the charcoal was essential, and that a fog was readily produced when a stream of air carrying hydrogen chloride was bubbled through an absorption flask containing an aqueous solution of sodium hydroxide. It was found, indeed, that the phosgene (or phosphorus oxychloride) was effective only by virtue of the hydrogen chloride arising from the hydrolysis by moisture in the charcoal (compare Bohart and Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 523). If a column of zinc dust (which absorbs hydrogen chloride but not phosgene) was interposed between the charcoal column and the absorption flask, the production of fog in the latter ceased. Further, if the charcoal was first freed from the greater part of its moisture by heating for some time at 160°, phosgene produced no fog under the original conditions.

Preliminary experiments also made it clear that the production of fog was not dependent on the presence of alcohol in the alkaline absorbent, although the presence of alcohol or other organic substances undoubtedly intensifies the fog. This matter is discussed in greater detail later.

The investigation accordingly resolved itself into a careful examination of (1) the conditions of bubbling under which this fog formation occurs, (2) the amount of fog and its dependence on the concentration of the alkali, (3) the effect of adding organic and colloid substances to the alkali, (4) the nature and concentration of the acid present in the fog particles, and (5) the size and possible electric charge of these particles.

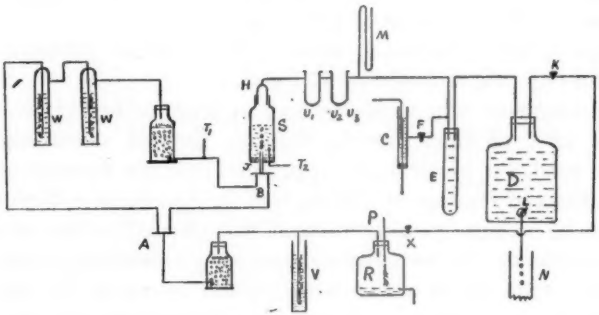
Experimental.

As a source of hydrogen chloride concentrated hydrochloric acid was used. Two wash-bottles, W (Fig. 1), were placed in series in

* The author's attention was directed to these facts by Prof. J. C. Philip.

a thermostat at 25·0°, and purified air from the reservoir, R, under a pressure of about 18 inches of water (kept constant by the water valve, V), was passed through the acid. The mixed gases, after being dried and filtered through several cm. of woolly asbestos in which the thermometer, T_1, was placed, passed to the three-way tap, B, and thence through the jet, J, to the vessel, S, which contained the alkaline solution and was fitted with a ground glass head, H, and an outlet tube. The fog was filtered out of the air by woolly asbestos in the tube U_1, which was kept in a box packed with cotton wool. (Special tests showed that the air from which the fog had been filtered out was free from chloride.) The moist air then passed to the tubes U_2 and U_3 containing calcium chloride. The dry air passed to the manometer, M, through the vessel, E, and then to the aspirator, D. The levels of the liquid in the limbs of

FIG. 1.



M were kept the same throughout an experiment. In cases of difficulty in maintaining this setting, the constant-level arrangement, C, was set in operation by opening the tap, F, whereby, if the pressure shown by M was less than atmospheric, water entered the graduated vessel, E, until atmospheric pressure was restored; the volume of water entering E was deducted from that run out of the aspirator.

The graduated indicator card attached to the tap, L, on D allowed of duplicate settings being made, although in all cases exact check of the rate of outflow was kept by means of a stop-watch. The filter pump, P, was arranged so that it could be used for suction from the aspirator by opening the tap, K. When this was not desired, the air to be pumped into R entered through the inlet, X, on the pipe line. The thermometer, T_1, gave the temperature of the entering gas and T_2 that of the solution.

The various vessels, S, were of such sizes that, by always using the same volume of solution, the " depths " of liquid, as measured

from the tip of the jet to the surface of the solution, were 7·5, 5·5, and 3·75 cm., respectively. Four jets were used, their radii being 1·81, 1·32, 1·08, and 0·82 mm., respectively. In order to prevent the solutions from creeping back into the barrels of the jets, the inside walls were coated with paraffin wax, but the tips were left clear.

All measurements of the rates of passage of the gas through the liquid are given in c.c. per minute. The alkali solutions were freed from carbonate, except where otherwise stated.

After the tube U_1 had been weighed, the asbestos was removed and extracted with water. The acidity as hydrogen chloride and the total chloride present were then estimated and invariably corresponded with one another. In the tables, "HCl %" refers to the percentage of acid by weight in the fog particles, both being given as mg. per litre of air. The standard quantity of air for an experiment was fixed at 2 l., as it was necessary to minimise the variation in concentration of the alkali.

Except where otherwise stated, the partial pressure of the hydrogen chloride is taken as 130 mm.

The amount of acid vapour which appears as fog varies between 0·8 and 12% of that passing through the jet, according to the solution used, the lower figure applying to simple aqueous solutions.

Conditions of Passage of Gas through the Solutions.—With aqueous solutions of sodium, potassium, and barium hydroxides an increase in the radius of the jet causes a greater production of fog, which, moreover, appears to attain a maximum at about 5·5 cm. depth, although, under similar conditions as to rate of passage, the amount of fog formed does not vary with depth by more than a few mg. per litre of air. In general, the concentration of acid in the particles is greatest when the depth of solution is 3·75 cm.

From Table I (giving mean values from 2 l. of gas), it will be seen that (1) the concentration of acid in the fog particles remains remarkably constant for a given jet; (2) the partial pressure of the water vapour in the air, after removal of the particles by the asbestos filter, is constant; and (3) increase in the rate of passage of the gas leads to an increase in the amount of fog. As the radius of the jet decreases and the depth of liquid increases, the relation between rate of passage and fog formation tends to become linear.

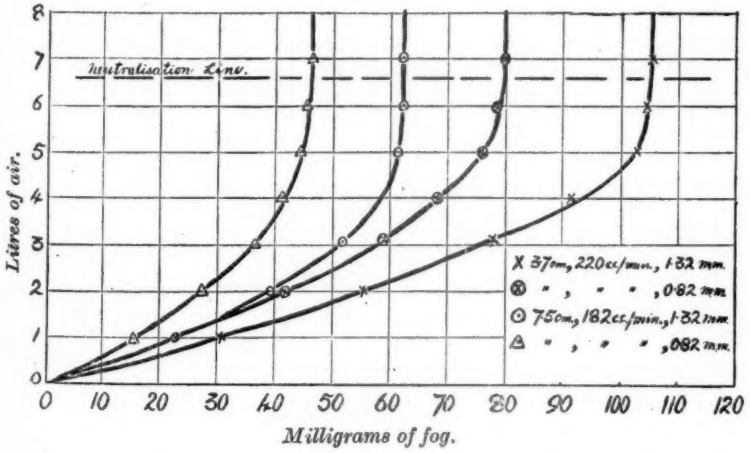
Concentration of Alkali.—Many experiments were made in which the same alkali solution was used until completely neutralised, the weight of fog formed being determined after each litre of air had been bubbled through the solution. As shown by Fig. 2 (for 0·614*N*-sodium hydroxide), the fog production falls off in every case as the alkali becomes weaker, and ceases when it is neutralised.

TABLE I.

Solution : 1·26*N*-NaOH. Depth : 7·5 cm. Air temp. : 20—23°.

Radius of jet, 1·81 mm.				Radius of jet, 1·32 mm.			
Rate (c.c./min.).	Fog (mg.).	HCl %.	Partial press. of H_2O (mm.).	Rate (c.c./min.).	Fog (mg.).	HCl %.	Partial press. of H_2O (mm.).
200	42·6	9·23	21·1	210	45·9	8·70	19·9
198	42·0	9·22	16·5	208	44·8	8·70	18·0
189	39·5	9·51	20·7	181	37·9	8·99	19·0
170	35·6	9·27	23·3	172	36·0	8·18	19·3
154	31·0	9·24	16·5	160	31·8	8·26	20·0
123	23·9	9·18	21·6	125	23·6	8·30	20·2
108	16·7	9·68	16·7	110	19·7	8·56	18·2

FIG. 2.



Solutions of potassium and barium hydroxides give similar results, although at corresponding concentrations less fog is obtained than with sodium hydroxide.

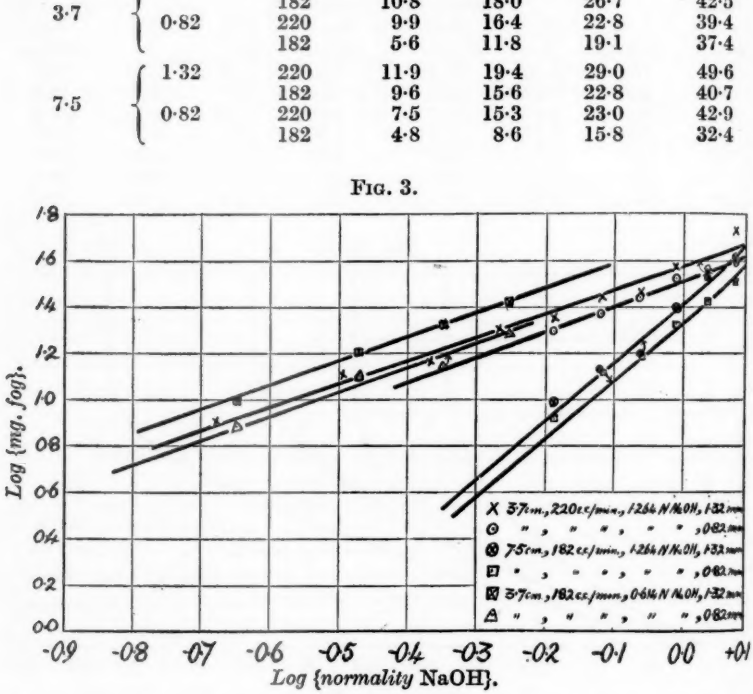
If the logarithm of the weight of fog obtained is plotted against that of the mean concentration of alkali during the passage of each litre of gas, a straight line is obtained. Moreover, under fixed conditions of depth and original concentration of alkali, the lines corresponding to the different jets are parallel, as shown in Fig. 3.

Table II shows the amount of fog formed at 20° (app.) in the first litre of air from different concentrations of sodium hydroxide (mean concentrations during each experiment). On plotting these figures it is seen that in dilute solutions the effect of the alkali is relatively great; in the more concentrated solutions, the amount of fog obtained is very nearly proportional to the alkali concentration.

TABLE II.

Depth of liquid (cm.).	Radius of jet (mm.).	Rate (c.c./min.).	Concentration. 0·07*N*.	0·26*N*.	0·56*N*.	1·21*N*.
3·7	1·32	220	14·0	22·2	30·9	49·2
		182	10·8	18·0	26·7	42·5
	0·82	220	9·9	16·4	22·8	39·4
		182	5·6	11·8	19·1	37·4
7·5	1·32	220	11·9	19·4	29·0	49·6
		182	9·6	15·6	22·8	40·7
	0·82	220	7·5	15·3	23·0	42·9
		182	4·8	8·6	15·8	32·4

FIG. 3.



In neutral or acid solutions of salts, dyes, and colloids (see later) and in water, in agreement with Fig. 2, all the hydrogen chloride is absorbed and no fogs are formed under the conditions of the present series of experiments. The incomplete absorption of the acid in alkaline solutions is not due to the rapid rates used, for in the presence of colloids and dyes thick fogs are obtained when only one bubble is formed every 2 or 3 seconds.

Solutions of the following salts of weak acids gave no fogs (in *N*-solution, except the diborate): Sodium acetate, sodium hydrogen carbonate, disodium hydrogen phosphate, sodium diborate (0·3*N*), and potassium dihydrogen phosphate. Thin fogs were formed with sodium carbonate and dense fogs with trisodium phosphate. The data in Table III were obtained for a depth of 7·5 cm. of solution, the rate being 225 c.c./min., the temperature 22°, and the jet radius 1·32 mm. They show clearly the changes in fog formation which

TABLE III.

Solution.	Air (l.).	Fog (mg.).	Solution.	Air (l.).	Fog (mg.).
N-Na_2CO_3.	1	9·7	N-Na_3PO_4.	1	25·5
	2	4·7		2	11·5
	3	4·1		3	1·3
	4	0·1		4	0·0

occur when the neutralisation has reached the hydrogen carbonate and disodium salt stages, respectively, and serve to emphasise the results of the foregoing experiments. Sodium carbonate is not so largely hydrolysed as trisodium phosphate and consequently its hydroxyl-ion concentration is somewhat less. This difference is plainly shown in the quantities of fog obtained. From the data in Table II, it is found that the concentrations of free sodium hydroxide which would give the same weight of fog under these conditions are 0·06N and 0·45N, respectively; these are of the order of magnitude which would be expected from the degrees of hydrolysis. It has not been possible to fix a definite value for the hydroxyl-ion concentration at which fog formation begins, but it must be greater than $10^{-5}N$, since the other phosphates and sodium bicarbonate give no fog.

Addition of Organic and Colloidal Substances to the Alkali.—Ethyl alcohol, amyl alcohol, acetone, formaldehyde, and ether, especially when present in considerable amount, gave dense fogs, but no fog was obtained in the absence of alkali.

Experiments were made with the following "capillary-active" substances: *iso*Amyl alcohol, sucrose, gelatin, gum arabic, safranine, methylene-blue (hydrochloride), Congo-red, Orange G, glycerol, saponin, kaolin, aquadag, and purified clay. Solutions (or suspensions) of these substances in sodium hydroxide were made, and the fogs formed under different experimental conditions were investigated. As a typical example the results for gelatin solutions in 1·24N-sodium hydroxide are given in Table IV, which also

TABLE IV.

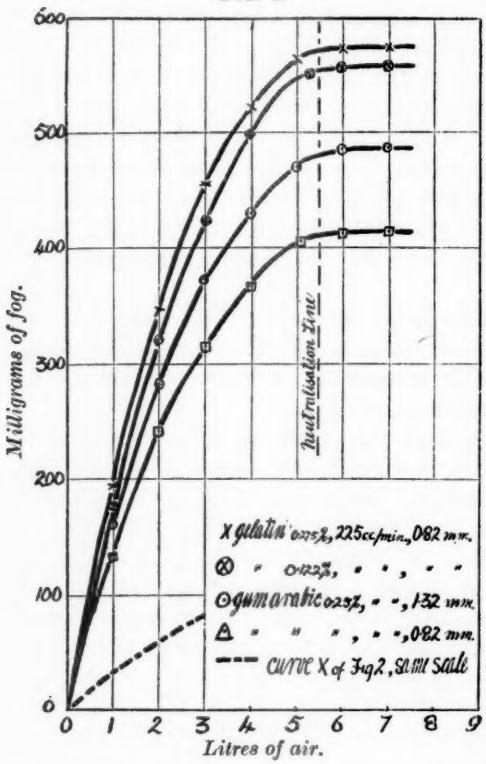
Rate: 208 c.c./min. Radius of jet: 1·32 mm. Depth: 7·5 cm.

Gelatin, %.	Fog (mg.).	Air temp.	Partial press. of H_2O (mm.).	Gelatin, %.	Fog (mg.).	Air temp.	Partial press. of H_2O (mm.).
0·0000	47·7	24·9°	21·7	0·041	141·4	25·8°	21·8
0·0032	63·0	25·3	21·9	0·081	153·8	25·1	22·2
0·0082	81·9	25·3	21·7	0·082	161·1	25·3	21·2
0·0163	102·9	25·7	22·3	0·098	167·3	23·9	19·7
0·041	137·7	24·5	22·3				

serves to show how constant and independent of the amount of fog formed is the aqueous vapour pressure of the air in contact with the particles.

In those cases where dense fogs are formed, the bubbles in passing up through the solutions become filled with fog and do not remain clear as in the case of the simple aqueous solutions. Addition of sodium chloride (0·5*N*) to the gelatin solutions caused a slight increase in the amount of fog formed, but small alterations in the concentration of the alkali did not have much effect. A peculiarity, which appears with other solutions also (see Fig. 5), was found with gelatin, *viz.*, that at about 110 c.c./min. the curve showing the relation between rate of passage of the gas and fog formation undergoes a sudden change of direction.

Fig. 4.


Milligrams of fog.
Litres of air.
Neutralisation line.
× gelatin 0·225%, 225 cc./min., 0·82 mm.
⊗ " 0·112%, " " "
⊙ gum arabic 0·25%, " " 1·32 mm.
△ " " " " " 0·82 mm.
--- curve X of Fig. 2, same scale

When the alkali solutions were treated with the air–hydrogen chloride mixture until neutralised, the concentration of acid in the particles was found to be practically independent of the stage of neutralisation. This was true, not only for gelatin but in general, for the other substances also.

As mentioned above, none of the solutions gave any fog after neutralisation. Comparison of the curves in Fig. 4 with those in Fig. 2 shows the great effect of adding colloidal substances to the solutions, and also the rapid decrease in fog formation as the solution becomes neutralised.

Safranine and methylene-blue were particularly active in fog formation. The pronounced effect of the latter, even in extremely dilute solutions, is shown in Table X. Sucrose, up to 5%, had no effect on fog formation; glycerol caused a decrease, probably owing to viscosity effects, as the solutions used were somewhat concentrated. All the other substances mentioned caused great increases in the amount of fog obtained.

When the data from which Fig. 4 was constructed were plotted in the same manner as used in Fig. 3, the curves were again linear. The slopes of these lines did not vary greatly with the capillary-active substance employed; thus, under corresponding conditions the lines for two solutions of differing gelatin content, for the gum arabic, and for the amyl alcohol solutions were almost parallel; with saponin, the results were somewhat irregular, but this is not surprising in view of the excessive formation of froth in this case. It will be seen later that, when the alkali concentration is kept constant and that of the added substance is varied, each substance has its own specific effect, *i.e.*, the slopes of the curves vary greatly according to the compound employed.

From the considerable amount of data obtained, it may be stated that: (1) The concentration of acid in the particles tends to decrease as that of the capillary-active substance decreases; *e.g.*, under similar conditions with a china clay in 0·343% and 0·206% suspensions, the concentrations of acid were, respectively, 8·32% and 7·83%, whilst in the case of methylene-blue a steady decrease in acidity occurred as the dye concentration decreased; (2) for a given concentration of capillary-active substance, the concentration of acid in the fog droplets is independent of that of the sodium hydroxide solutions, *e.g.*, with gelatin in 0·61*N*- and 1·24*N*-sodium hydroxide, the acid concentrations are the same for fogs formed under similar conditions; and (3) the partial pressure of aqueous vapour in the air surrounding the particles is constant and independent of the amount of fog formed.

Experiments with Hydrogen Bromide.—Hydrogen bromide, although much more active than the chloride, resembles it in giving no fog with water or with neutral or acidic salt solutions.

The experiments with colloids in 0·59*N*-sodium hydroxide solution (Table V) were carried out under the following conditions: Radius of jet, 1·32 mm.; rate, 208 c.c./min.; depth of liquid, 7·5 cm.; air temperature 21·0—21·8°.

TABLE V.

Colloid.	Air (l.).	Fog (mg.).	HBr, % (mean).	Part. press. of H_2O (mm.).
Gelatin (0·122%).	1	180·2	21·8	21·2
	2	164·1		22·0
	3	132·6		21·6
	4	106·3		20·1
Gum arabic (0·25%).	1	148·7	21·9	18·6
	2	133·5		20·6
	3	114·3		20·6
	4	89·7		20·4

The % of hydrogen bromide in the particles is very large, but constant whether colloids are present or not; expressed as normal-

ities, however, the concentrations are nearly the same as (in fact, a little higher than) in the case of hydrogen chloride.

The relation between alkali concentration and fog formation is the same as for hydrogen chloride, and when plotted, the lines for gelatin and gum arabic are practically parallel.

The partial pressures (about 59 mm.) of the hydrogen bromide in the air and acid mixtures in these experiments were considerably lower than with hydrogen chloride, yet the amount of fog formed under similar conditions was greater; this is probably due to the slower diffusion of the hydrogen bromide.

Alcoholic Solutions.—The weaker solution used did not give very dense fogs, but the stronger gave very dense ones; in the latter case, the bubbles, as they passed up through the solution, were filled with fog. With strong alcoholic solutions, the narrower the jet the greater is the amount of fog obtained. This is the reverse of that found for the simple aqueous solutions.

The solutions contained 7·6% and 33·0% by weight of alcohol, respectively, and were 1·223*N* and 1·238*N* with regard to sodium hydroxide.

The alcohol in the fogs was estimated by Benedict and Norris's method (*J. Amer. Chem. Soc.*, 1898, **20**, 293), in which a standard solution of potassium dichromate in concentrated sulphuric acid is used for oxidation, but since the presence of chloride in the solutions caused high results, the following modification was adopted. After extraction of the asbestos with water, the volume being kept as small as possible, the washings were run into a graduated flask to which an excess of 0·03185*N*-silver sulphate solution was added; after standing and being shaken for some time, the liquid was made up to volume. Portions were then filtered off for estimation of alcohol and of the excess silver. From the gross amount of alcohol found on analysis, a deduction was made for alcohol adsorbed by the asbestos, the latter having been determined by separate experiments.

An attempt was made to estimate separately the partial pressures of the alcohol and water vapours in the gas after filtering out the fog. Fresh calcium carbide, as described by Thomas (*J. Soc. Chem. Ind.*, 1922, **41**, 33T), was used for this purpose. The change in weight of a U-tube filled with carbide multiplied by 2·91 (experimental factor determined by blank experiments) gave the weight of water vapour in a given volume of air; the alcohol was absorbed in concentrated sulphuric acid, which, as shown by blank experiments, did not absorb acetylene. Hence the partial pressures of the water and alcohol vapours could be calculated.

The fogs produced at each stage of the neutralisation of the

stronger solution were analysed: the composition of the particles with regard to both alcohol and acid content remained constant.

Series of experiments similar to those already described for other solutions were carried out. As shown in Fig. 5, there is a critical rate below which the amount of fog formed falls off rapidly as the rate decreases. Some of the results are in Table VI. It is seen that the lower the alcohol concentration the greater is the % of

TABLE VI.

Solution: Aqueous alcohol, NaOH 1·23-*N*. Depth of liquid: 7·5 cm.
Air temp.: 20·4—22·5°.

Alcohol, %.	Radius of jet (mm.).	Rate (c.c./min.).	Fog (mg./l. of air).	HCl, %.	Alcohol in fog, %.	Part. press. (mm.) Alcohol.	Part. press. (mm.) H_2O.
7·6	1·32	191	44·7	8·42	9·40	7·86	24·8
		154	37·6	7·67	9·51	6·60	19·5
		149	35·8	7·77	9·76	7·11	22·4
		118	30·1	7·90	8·75	7·82	21·4
		101	24·0	10·59	10·85	6·50	21·6
33·0	0·82	222	132·7	5·16	41·9	18·2	—
		195	130·4	5·23	45·0	18·0	24·8
		192	127·8	5·11	44·4	18·2	24·9
		159	118·8	5·25	43·9	20·4	—
		126	113·2	4·94	43·6	21·2	22·3
		126	112·1	5·02	43·9	21·0	25·7
		74·5	76·6	4·85	41·8	21·4	20·9

acid in the fog particles. Moreover, the percentages of alcohol in the fog particles are somewhat greater than those in the original solution. In view of the work of Kablukow (*Z. physikal. Chem.*, 1903, **46**, 399), however, it is probable that the vapour given off by the alkaline solutions is richer in alcohol than that given off by a simple aqueous solution of the same alcohol content. If a correction is applied to the usual vapour-composition data, assuming that sodium hydroxide has the same effect on the vapour composition as potassium iodide, it is found that the % of alcohol to be expected in the liquid in equilibrium with that vapour is close to that actually found.

Some experiments summarised in Table VII show what changes take place in a fog when bubbled through a second wash-bottle; in the examples given, the solution was 1·24*N*-sodium hydroxide in 50% (by vol.) alcohol. The symbols I and II refer to the first and

TABLE VII.

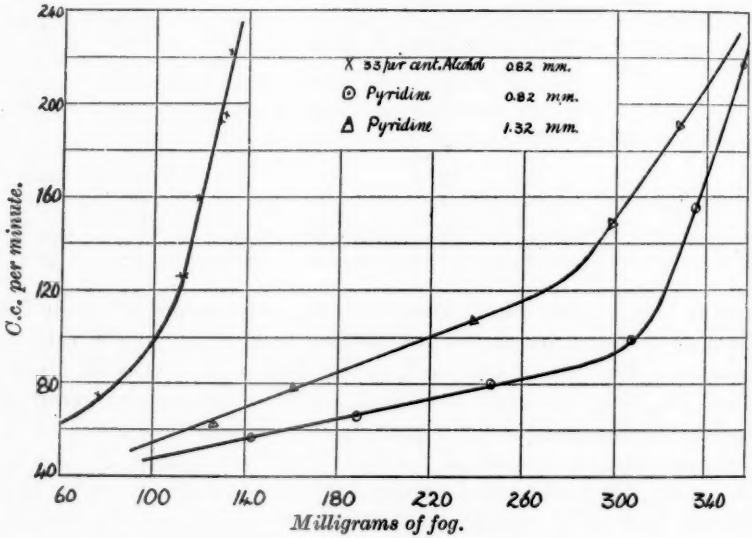
Radius of jet (mm.). I.	Radius of jet (mm.). II.	Rate (c.c./min.).	Fog (mg.). I.	Fog (mg.). II.	Absorption, %.	HCl in fog, %. I.	HCl in fog, %. II.
0·60	0·99	200	172	89·2	48·6	5·2	2·00
0·60	0·99	219	187	105·1	43·9	5·2	2·00
1·66	0·60	200	145	40·8	71·8	4·5	1·60

second wash-bottles, respectively. These figures clearly show how much more effective the narrower jets are for causing absorption of the particles. A great decrease in acid concentration is shown also, which can only be explained by condensation of vapour on the particles; whether this condensation is preferential or not has yet to be determined.

The alcoholic solutions follow the logarithmic law put forward in connexion with the other solutions.

Pyridine Solutions.—Pyridine was used to see whether an organic base would give fogs under the experimental conditions. (Aniline behaves in a similar manner to pyridine.) With an $M/2$-solution,

FIG. 5.



very dense fogs were obtained in which the concentration of acid varied somewhat more than usual with the rate of passage of the gas, decreasing with decrease in the rate. The critical rate of about 110 c.c./min. is shown very distinctly in Fig. 5. During progressive neutralisation of the base, the concentration of acid in the particles remained steady, as also did the partial pressure of aqueous vapour. In this case also, as with the stronger alcoholic solution, the narrower jet was the more effective fog producer.

The pyridine solution follows the same law as do the simple aqueous solutions during the process of neutralisation.

The use of pyridine is complicated by its volatility, and this no doubt is one reason that fog was formed in the bubbles as they passed through the solution. This aspect of the question has been

examined qualitatively, using solutions of ammonia and of hydrogen chloride of varying concentrations. If air carrying hydrogen chloride is passed through ammonia solutions, fogs are formed in all cases because even in dilute solutions ammonia has an appreciable vapour pressure. If, however, the vapour from even concentrated ammonia is passed through hydrochloric acid solutions, no fog is obtained until an acid solution is used of such high concentration that the partial pressure of the chloride rises above its infinitesimally small values in the dilute solutions. The formation of fogs begins in about 18% acid, and their density increases rapidly as the concentration of the acid rises above this.

Sizes of, and Charges on, the Particles.—Since the partial pressure of the water vapour and the concentration of acid in the fog particles remain practically constant, it would be expected, assuming the system to be in equilibrium, that the particles would all have the same radius, but this expectation is not completely fulfilled.

The apparatus used for studying the size of the fog particles consisted of an inner cylinder of thin, hard glass, surrounded by a thick one, the space between being sealed at each end. Wide-bore taps were used to minimise contact of the fog with surfaces. Light entered on one side by a narrow slit; on another slit at the front the level of the fog surface was read at intervals. The surface of the fog remained level during an experiment except when the densest fogs were being used.

The Stokes–Cunningham equation was used for calculating the radius of the particle from its rate of fall. The equation may be reduced to the form $r = x\sqrt{v}$, where r is the radius in cm., v is the velocity of fall in cm./sec., and x varies according to the viscosity of the medium and the density of the particle. For the aqueous, alcoholic (7·6 and 33·0%), and pyridine solutions with hydrogen chloride, and for the aqueous solutions with hydrogen bromide, x has been given the values 8·92, 9·00, 9·23, 8·92, and $8{\cdot}40 \times 10^{-4}$, respectively, the corresponding densities of the particles having been taken as 1·04, 1·02, 0·97, 1·04, and 1·17.

Experiment showed that the particles had the same radius at all stages of the neutralisation of the solution, but they increased somewhat rapidly in size during the time of settling, this being particularly noticeable in the case of those from the alcoholic solutions. With dense fogs, the particles appear to be smaller than in the other cases. Table VIII gives the radii of a number of dense fogs, 0·62*N*-sodium hydroxide being used (except with pyridine).

In general, the particles became larger as the concentration of

TABLE VIII.

Depth of liquid: 7·5 cm. Radius of jet: 1·32 mm.

Substance.	Conc.	Rate (c.c./min.).	Temp.	Radius (cm.) × 10^4.
Methylene-blue ...	0·02%	210	25·3°	1·62
,, ,, ...	0·004%	210	24·7	1·41
Gelatin	0·122% (with 0·5*N*-NaCl)	210	22·5	1·08
Buxton clay	0·186%	210	25·3	1·19
Pyridine	*M*/2	208	25·5	0·50—1·16
,, ...	,,	77	23·8	—1·19

colloid, etc., decreased, as the radius of the jet decreased (rate constant), and as the rate decreased (radius of jet constant). With the alcoholic solutions, the particles given by the stronger solution were somewhat smaller than those given by the weaker. In all cases the particles in the hydrobromic acid fogs were smaller than those obtained under similar conditions with hydrochloric acid.

From the various data obtained, it appeared that the original size of the particles is possibly of the same order as for fogs from other reactions, *viz.*, 5×10^{-5} cm.,—pyridine has given particles originally of radius 5·0—7·2 $\times$ 10^{-5} cm., methylene-blue of 7 $\times 10^{-5}$ cm. These, however, are very unstable, often increasing rapidly to a mean radius of 2×10^{-4} cm. Whether the comparatively large particles (2—3 $\times$ 10^{-4} cm.) of the fogs from the simple aqueous solutions have grown from smaller particles, it is not possible to say. Apparently an equilibrium state is reached by the particles, since the partial pressure of the water vapour and the concentration of acid remain nearly constant and independent of the conditions of formation. It is hoped to investigate this matter further.

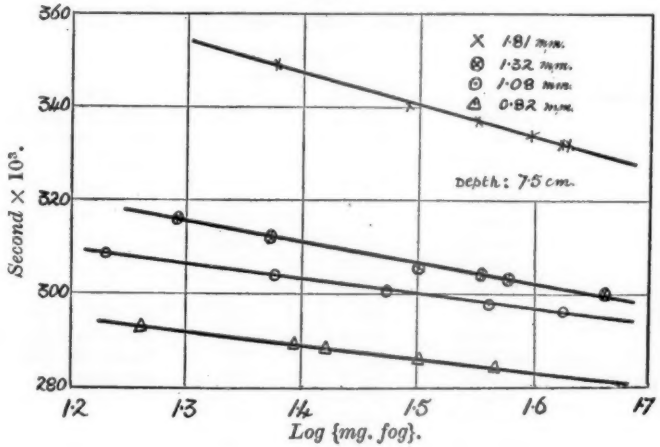
An attempt was made to determine the charges on the particles, but no definite evidence was obtained as to the presence of such charges. This is not surprising in view of the work of Bloch (*Ann. Chim.*, 1911, **22**, 370, 441; **23**, 28), who found that many organic liquids decreased or completely inhibited the formation of charges in a gas bubbling through aqueous solutions in which they were dissolved or on which they formed a layer.

Discussion.

For the rate of absorption of hydrogen chloride (or bromide) from bubbles containing the acid vapour we have $dw/dt = AKP_g$, in which A is the area of the bubble, P_g the partial pressure of the gas, and K the over-all diffusion constant (Lewis and Whitman, *Ind. Eng. Chem.*, 1924, **16**, 1215). Now $dw = -X \cdot dP$, where X is a function of the molecular weight of the gas; hence, $dP/dt = -AKP_g/X$, or $\log_e P_0/P_t = AKt/X$, where P_0 and P_t are the pressures at times 0 and t. Since in these experiments P_0 and the con-

centration of acid in the particles are constant, the equation becomes $K'' - K't = \log_e F$, where K'' and K' are constants, and F is the number of mg. of fog per litre of air. This requires that the relation between the time of contact of the bubbles with the solution and the logarithm of the weight of fog should be linear. Fig. 6 shows that this requirement is fulfilled. At the depth of 7·5 cm., as shown in Fig. 6, the lines get slightly steeper as the radius of the jet increases, but it has been found that the similar lines drawn for the depths 3·7 cm. and 5·5 cm. are practically parallel. Moreover, there is not a great difference between the slopes of the lines whatever the size of jet or depth of liquid.

FIG. 6.



On plotting the data obtained in the experiments where the concentration of capillary-active substance was varied, it is found that straight lines are obtained (Fig. 7) corresponding to the general equation $\log_{10} F = m \log_{10} C + K_1$, in which F is the weight of fog (in mg.) formed in the first litre of air used, C is the concentration % of added material, and m and K_1 are constants. The values thus found for m and K_1 for various solutions are given in Table IX, and some typical experimental and calculated values in Table X. It will be seen that the above expression satisfactorily represents the experimental results except for a few very dilute solutions.

The activities of the substances used extend over a wide range; the only generalisation which emerges is that basic substances (*e.g.*, safranine and methylene-blue) are more active than others (*e.g.*, gum arabic and Congo-red). The constant K_1 may be defined as the logarithm of the amount of fog which would be obtained

TABLE IX.

Substance.	Conc. of alkali (*N*).	*m*.	K_1.	Substance.	Conc. of alkali (*N*).	*m*.	K_1.
*iso*Amyl alcohol	0·59	0·274	1·938	Safranine ...	0·61	0·446	2·852
Gelatin	0·61	0·284	2·532	Congo-red ...	0·61	0·385	2·237
Gelatin	1·24	0·287	2·522	Orange G. ...	0·61	0·370	2·326
Gelatin +0·5*N*-NaCl	0·61	0·240	2·504	Kaolin (1) ...	0·61	0·508	2·080
Methylene-blue	0·61	0·218	2·700	Kaolin (2) ...	0·61	0·385	2·169
				Aquadag (1)	0·61	0·286	2·352
				Aquadag (2)	0·61	0·390	2·667
				Buxton clay	0·61	0·212	2·510

Kaolin and Aquadag (1): partial pressure of HCl, 36·7 mm.
" " " (2): " " " 139·2 "

TABLE X.

Solution: 0·61*N*-NaOH.

Substance.	%.	Fog (mg.). Found.	Calc.	Remarks.
Gelatin.	0·098	171·8	176	Points are scattered on both sides of the line drawn.
	0·073	156·2	162	
	0·052	142·4	147	
	0·049	143·2	145	
	0·024	123·8	118	
	0·008	87·1	87	
	0·0035	70·5	68	
	0·0016	52·9	54·5	
	0·000	23·4	—	
Methylene-blue.	0·0267	222·8	227	The last two points fall below the values required by the straight line.
	0·0133	195·0	195	
	0·0067	168·1	168	
	0·0027	146·7	138	
	0·0013	117·5	117	
	0·00067	98·1	102	
	0·00027	66·0	83	
	0·0000	31·9	—	
Aquadag (1).	0·194	142·0	141	All the points lie close to the line drawn through them.
	0·130	124·5	126	
	0·065	103·5	103	
	0·039	88·7	89	
	0·026	80·6	79	
	0·013	61·7	65	
	0·000	17·1	—	

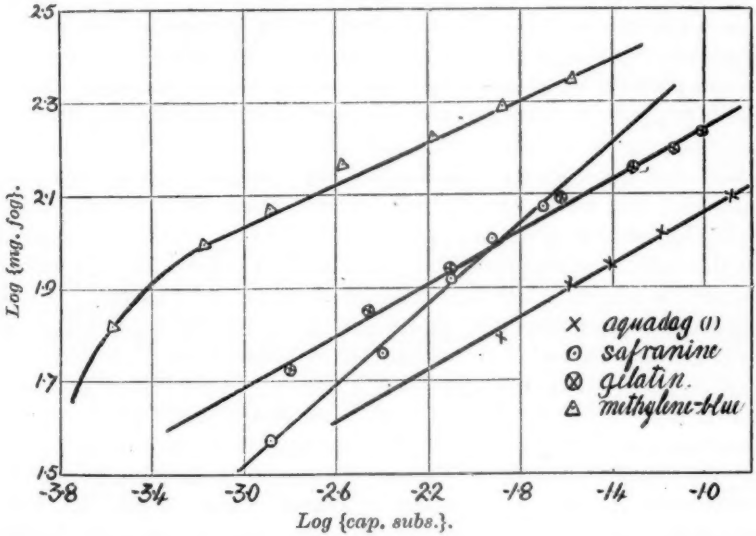
from a 1% solution, provided that the straight-line law held up to that point; K_1 is thus a measure of the activity of the given material. Fig. 7 shows that the slope of each line is a specific property of the corresponding substance, *i.e.*, that the rate of change of fog formation with change in concentration varies from one material to another.

The great capillary activity of such substances as gelatin and methylene-blue has been noticed in other directions (Donnan, *Rep. Brit. Assoc.*, 1923, Sect. B, 12), *e.g.*, *E.M.F.* (Šendera, *Rec. trav. chim.*, 1925, **44**, 480), cataphoresis (van der Grinten, *J. Chim.*

physique, 1926, **23**, 209), water-fall experiments (McTaggart, *Phil. Mag.*, 1914, **27**, 297). As the relation between the amount of material present and the effect it produces is of the same form as the "adsorption isotherm," it has generally been concluded that adsorption at the interface is the cause of the phenomena. The equation given above has the same form as the adsorption isotherm.

It is rather remarkable, however, that such great effects should be obtained, since the surface tensions of these solutions differ very little from that of pure water or of the alkali solutions used. That surface tension is probably not the controlling factor, at any rate

FIG. 7.



so far as fog formation is concerned, is shown by the fact that although amyl alcohol causes great reductions in surface tension it is not very active as regards fog formation.

A survey of the possible causes of the decreased rate of absorption of the acid vapours brings out the fact that the seat of the phenomenon lies in the film round the bubble, and that this film is greatly altered by colloids, etc. Moreover, the peculiar properties of this film only appear in alkaline solution. A case of inhibited diffusion of a gas through an alkaline film has been noted by Taylor (*Fuel*, 1926, **5**, 195); in this case, the whole system was wet, so that it is not possible to say whether this film behaved towards water vapour in the same way as the alkaline films round the gas bubbles behaved in the present experiments.

A serious problem is that of explaining how all the moisture gets into the bubbles in order to form the great quantities of fog obtained in some cases. It may be that the film acts as a membrane which is readily permeable to water vapour but not so permeable to the acid gas.

In some of the experimental data it is noteworthy that the vapour pressures recorded are greater than correspond to saturation for air at the temperatures given. This is probably connected with the uncertainty attaching to the temperature, for it is difficult to control the heat effects arising from (i) the neutralisation process in the solution, and (ii) the condensation of water to form the fog particles. This uncertainty causes a complication in the attempt to correlate the size of the particles with their acid content. Rothmund (*Monatsh.*, 1918, **39**, 571) used an approximate form of the equation connecting vapour pressure with the radius of curvature of the particle by equating the increase in vapour pressure, due to the increased curvature, to the decrease brought about by dissolved material. The equation obtained finally was $r = 6{\cdot}1 \times 10^{-6}/ci$, where r is the radius of the drop, c the concentration of dissolved material, and i the van 't Hoff factor. With Rothmund's ozone fogs, the formula gives results of the right order, but if it is applied to the results of the present author and of others, the calculated values for the radii are very wide of those actually found. It is a remarkable fact that fog and cloud particles (whether liquid or solid), when formed by spontaneous condensation of vapour, all tend to have a radius of about 5×10^{-5} cm. None of the equations which have been put forward (such as Rothmund's given above, von Weimarn's equation of state, or the equation connecting vapour pressure and radius of curvature) gives any indication of such a "critical" radius. Donnan (*Z. physikal. Chem.*, 1903, **46**, 197) has deduced thermodynamically, however, that a critical radius of about 1×10^{-5} cm. should exist, and Lewis ("System of Physical Chemistry," 1920, I, 332) shows that with oil emulsions there is a distinct tendency for the particles to approximate to this size; but that the same radius should be found general for aerial colloids is certainly remarkable. The comparatively large particles found in the present experiments are probably the result of condensation of vapour on particles originally of this critical radius.

Many of the data recorded in the present investigation suggest that the fog droplets persist even in an unsaturated atmosphere. This is not unexpected, as it is well known that mists formed in the presence of ions can exist for long periods in highly unsaturated atmospheres. But in the present case the uncertainty as to temperatures precludes any definite conclusions on this matter. Further

and more accurate information on this and other factors is required before the conditions of stability of these fogs can be completely understood.

Summary.

1. It has been shown that hydrogen chloride and hydrogen bromide vapours are incompletely absorbed by alkaline solutions, more particularly in presence of colloids and dyes. A limiting concentration of hydroxyl ions probably exists below which absorption is complete.
2. The relations between the amount of fog formed and alkali concentration, and also between the amount of fog and the concentration of capillary-active substance, are logarithmic and of the same form as the "adsorption isotherm."
3. The concentration of acid in the fog particles and the partial pressure of the water vapour in contact with them are practically constant.
4. The radii of the particles are smaller the denser the fog produced.
5. No electrical charges have been definitely detected.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CXXXVII.—*The Purification of Acetic Acid. The Estimation of Acetic Anhydride in Acetic Acid.*

By KENNEDY JOSEPH PREVITÉ ORTON and ALAN EDWIN BRADFIELD.

THOUGH the purity of commercial acetic acids has undergone considerable improvement within the last three or four years, it is still found to be necessary to distil from 2% of chromic oxide, as described by Orton and Bradfield (J., 1924, **125**, 960), in order to obtain an acid free from reactive impurities suitable for a medium for the delicate halogenation experiments which are in progress in this laboratory. The resulting stable acetic acid melts, however, some 0·5° lower than the original acid, owing to the formation of water by oxidation of the impurities, and to obtain an acid melting above 16°, the rather tedious and wasteful process of fractionation was resorted to. It is now found that when acetic anhydride

equivalent to the water present is added together with the chromic acid, by simple distillation some 85% of a commercial acid melting at, say, 14·5—15·5° can be converted into a stable acid melting at 16·2—16·4°.

It was shown by Orton and M. Jones (J., 1912, **101**, 1708) that, unless a catalyst be present, the hydrolysis of acetic anhydride in glacial acetic acid is a slow process, but that strong acids have a powerful catalytic effect. The chromic acid used in the above process acts as the necessary catalyst so effectively that the distillate contains not more than 5 parts of acetic anhydride per 100,000, an amount which is generally negligible, and gradually falls to zero on keeping.

The following illustrates the method. A commercial acetic acid melted at 14·2°. If distilled from chromic oxide alone, a main fraction melting 0·5° lower, *i.e.*, at 13·7°, would be obtained. If the melting point of the anhydrous acid be taken as 16·6°, and the lowering of the melting point as 0·2° for each 0·1% of water present (de Visser, *Rec. trav. chim.*, 1893, **12**, 101), this would correspond to 1·45 g. of water per 100 g. of acid. To each 100 g. of acid were therefore added $1{\cdot}45 \times 102/18 = 8{\cdot}22$ g. of acetic anhydride, and 2 g. of chromic oxide. The mixture was heated to just below the boiling point for ½ hour, and then distilled, a short still-head being used to prevent traces of chromic acid being carried over as spray. A first fraction of 10—15% was neglected; the remainder, collected as one fraction, melted at 16·2°, had a bromine absorption number of 1·1 (Orton and Bradfield, *loc. cit.*), and, tested as described below, was found to contain 0·0047 g. per cent. of acetic anhydride. An acid purified in this manner which had been standing for 3 months contained no trace of acetic anhydride. It should be noted that if halogen is present in the original acetic acid, chromium will appear in the distillate.

For the rectification of an acid previously distilled from chromic acid alone, distillation in a similar way of a mixture with the theoretical amount of acetic anhydride (no further lowering of melting point of 0·5° being allowed for in this case) together with 0·2 g. per cent. of β-naphthalenesulphonic acid as a catalyst, is equally effective.

A further examination of the effect of possible impurities on the "absorption" of chlorine and bromine by acetic acid indicates that the high "absorption number" for bromine shown by commercial acids is probably due mainly to formic acid, whilst the presence of 0·15 g. per cent. of acetone causes an appreciable absorption of chlorine. The presence of a manganese salt or of ethyl alcohol has little effect.

The Estimation of Acetic Anhydride in Acetic Acid.—In 1911, Orton and Edwards (J., **99**, 1181) developed a method of estimation of acetic anhydride in acetic acid based on the knowledge that 2 : 4-dichloroaniline is rapidly and completely acetylated by acetic anhydride, whilst, at the ordinary temperature, acetic acid is without action. The method has been modified by Spencer (*J. Assoc. Offic. Agric. Chem.*, 1923, **6**, 493), who used ordinary aniline in place of the 2 : 4-dichloroaniline, and after separation of the aniline and anilide by a method similar to that employed by Orton and Edwards, titrated the anilide, after hydrolysis, with a bromate–bromide solution; and by Calcott, English, and Wilbur (*Ind. Eng. Chem.*, 1925, **17**, 942), who used the dichloroaniline, and titrated the excess with nitrous acid.

In the present modification, 2 : 4-dichloroaniline is added to the acetic acid, containing anhydride, and the excess aniline estimated by titration with bromate–bromide solution, without separation from the anilide formed. To 75 c.c. of the acid to be tested, 10 c.c. of a solution of 2 : 4-dichloroaniline in acetic acid (containing approximately 3 g. in 250 c.c.) were added. Next morning, the solution was diluted with 85 c.c. of water, 10 c.c. of 10% hydrochloric acid were added, and then 10 c.c. of 1·862*N*/10-bromate–bromide solution. The flask was corked, and potassium iodide added after 5 minutes. 9·60 C.c. of 1·005*N*/20-thiosulphate were required. In a control, in which 75 c.c. of an acid known to contain no anhydride were used, and the other quantities and the procedure were the same, the titre was 8·43 c.c. of 1·005*N*/20-thiosulphate. Hence the aniline acetylated is equivalent to $(9{\cdot}60 - 8{\cdot}43) \times 1{\cdot}005$ c.c. of *N*/20-bromine, and the acetic anhydride = 0·004 g. per 100 c.c. (Br_2 equivalent $C_6H_3Cl_2{\cdot}NH_2$).

The method was tested by the titration of the aniline in the presence and the absence of 2 : 4-dichloroacetanilide, and more rigorously by the addition of known quantities of acetic anhydride to acetic acid, and actual estimation thereof. The following results were obtained :

Anhydride (g.) added to 75 c.c. of acid.	Anhydride found. (a).	(b).
0·0955	0·0936	—
0·0478	0·0479	0·0470
0·00955	0·00951	0·00942

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CXXXVIII.—*The Chlorination of Anilides. The Directing Influence of the Acylamido-group.*

By KENNEDY JOSEPH PREVITÉ ORTON and ALAN EDWIN BRADFIELD.

Proportions of the Isomerides formed by Chlorination.

IN 1909, Orton and W. Jones (J., 1909, **95**, 1056) showed that the chlorination of acetanilide, in acetic acid solution, by the addition of the calculated quantity of bleaching powder solution yielded some 40% of *o*-chloroacetanilide, the remainder of the acetanilide being converted into the *p*-isomeride. This investigation was extended to other acylanilides by Orton and King (J., 1911, **99**, 1377). These authors aimed at an actual separation of the products of chlorination by a process of crystallisation of the anilides and fractional steam distillation of the anilines obtained by hydrolysis, and estimated the proportions of the isomerides formed from the yields of pure substances obtained. In addition, Orton and King (J., 1911, **99**, 1369) measured the velocity coefficients for the reaction between various anilides and chlorine.

On reviewing these results subsequently, it was felt that some uncertainty would attach to any deduction, bearing on the problem of the directing influence of the acylamido-group on nuclear substitution, made by a correlation of these two series of measurements, since the estimate of the proportions of the isomerides formed was not so satisfactory as could be desired, for the reasons stated below. First, the method of chlorination involves the gradual dilution of the acetic acid medium by the bleaching powder solution used for chlorination, so that in the experiments referred to the medium varied from 100% to 50% acetic acid as the chlorination progressed. The results obtained by Holleman, Hartogs, and van der Linden (*Ber.*, 1911, **44**, 704) showing the marked effect of medium on the nitration of anilides suggest that the values obtained for the proportions of *o*- and *p*-chloro-compounds may actually represent a kind of average for more or less dilute acetic acid medium. Secondly, the actual isolation of the isomerides in a pure state involves a number of processes, which from their nature cannot be carried out in an exactly quantitative way. A re-determination was therefore undertaken.

In the present series of experiments, the composition of the chlorination product of acetanilide was determined by the freezing-point method, without any attempt at preliminary separation, and confirmed by a quantitative separation by sublimation of the *o*- and *p*-chloroacetanilides, a process which is very readily carried out.

In experiments on other acylanilides, these were first hydrolysed, and the anilines acetylated for analysis.

The delicate method of chlorination introduced by Orton and King (J., 1911, **99**, 1185), based on the reversible reaction between a chloroamine and hydrochloric acid,

$$>NCl + HCl \rightleftharpoons Cl_2 + >NH,$$

lends itself admirably to the present purpose. With many chloroamines, in glacial acetic acid, the equilibrium lies almost entirely to the right, and since the equilibrium is attained almost instantaneously, the addition of hydrochloric acid to a solution of a chloroamine results in the liberation of an exactly measured quantity of chlorine at the moment required. Moreover, since nucleus chlorination results in the liberation of hydrochloric acid equivalent to the chlorine used, the addition of a trace of hydrochloric acid suffices for complete chlorination, thus avoiding a high concentration of chlorine at any period of the reaction and the formation of anilide hydrochlorides in anhydrous solutions.

For the chlorination of acetanilide, the chloroamine most suitable as a source of chlorine is that of acetanilide itself, *i.e.*, the reaction is most readily carried out by allowing *N*-chloroacetanilide to undergo the so-called " transformation " (Orton, *Brit. Assoc. Reps.*, 1910, 85) :

$$C_6H_5\cdot NClAc \longrightarrow C_6H_4Cl\cdot NHAc\ (o- + p-).$$

The possibility presents itself that at the moment of liberation of chlorine from *N*-chloroacetanilide, the acetanilide molecule may be in a special " reactive " state, and that the proportions of the isomerides formed may differ from those formed when the chlorine is not generated in this way. This, however, is not the case, as is seen from Table I, where the mean values from several experiments for the percentage of *p*-chloroacetanilide formed by the " transformation " of *N*-chloroacetanilide and by the chlorination of acetanilide by chlorine derived from another chloroamine are given for different media. The remainder of the product is the ortho-compound in each case.

TABLE I.

Chlorination at 20°.

	Percentage of para.	
Medium.	Chlorination of acetanilide.	Transformation of *N*-chloroacetanilide.
Chloroform	68·8	69·8
Acetic acid	67·5	66·8
50% Acetic acid	60·7	57·3
Methyl alcohol	60·6	—

It is seen from the above table that the medium has only a small effect on the proportions of *o*- and *p*-isomerides. No explanation is at present offered to account for the differences between the values for 50% acetic acid, which seem to be rather greater than the experimental error involved.

In Table II is shown the percentage of the isomerides formed by the chlorination of several anilides. The most striking feature of these results is that although the acids corresponding to the acyl groups differ so largely in strength as measured by their ionisation constants, in molecular weight, and in "space-filling power," yet the proportions of the isomerides are practically the same in each case.

TABLE II.

Chlorination in acetic acid, m. p. 16°, at 20°.

Anilide.	% ortho.	% para.
Formanilide	30·1	69·9
Acetanilide	32·5	67·5
Benzanilide	30·4	69·6
Benzenesulphonanilide	35·0	65·0

Similarly, the nitration of formanilide, acetanilide, and benzanilide under the same conditions yields approximately the same proportions of *o*- and *p*-nitroanilides (Holleman, Hartogs, and van der Linden, *loc. cit.*).

Velocity of Chlorination of Anilides.

Orton and King (*loc. cit.*) found it possible to employ their method of chlorination for the measurement of the velocity of the reaction between chlorine and anilides in acetic acid solution, a reaction which is found to be of the simple bimolecular type. Their measurements are for an acetic acid containing 0·14% of water, as a medium, at a temperature of 16°. The velocity of chlorination is found to be very sensitive to the medium effect of water, increasing rapidly as the proportion of water is increased.

The experiments described above on the proportions of the isomerides formed were carried out at 20°, in an acetic acid, m. p. 16°, *i.e.*, containing about 0·3% of water. The velocity determinations have been repeated at 20°, in a medium containing 1% of water, the errors due to slight variation in the water content being thereby minimised. Column 1 of Table III gives the velocity coefficients at 20° for perfectly standard conditions, namely, anilide and chlorine both initially at 0·0025 mol./litre; hydrochloric acid 0·0125 mol./litre; medium, acetic acid with 1% of water. In column 2 are Orton and King's values for these and other anilides, and in column 3 the ionisation constants of the acids $R{\cdot}CO_2H$, corresponding to the groups $R{\cdot}CO{\cdot}NH-$, are given for reference.

TABLE III.

Velocity coefficients.

Anilide.	O. and B. (H_2O = 1%).	O. and K. (H_2O = 0·14%).	Ionisation constant of $R{\cdot}CO_2H$. $K \times 10^5$.
Formanilide	9·2	4·95	21·4
Acetanilide	62·2	40·0	1·86
Propionanilide	—	72·0	1·34
Butyranilide	—	64·5	1·49—1·75
*iso*Valeranilide	—	57·0	1·67—1·73
Benzanilide	69·1	42·0	6·8
Benzenesulphonanilide	42·7	—	—

The amount of hydrochloric acid employed produces an appreciable effect on the velocity of chlorination, the effect on acetanilide being a decrease in speed as the hydrochloric acid is increased, although with formanilide and benzenesulphonanilide this effect is reversed (see Table IV). The validity of the correlation of the velocity measurements under standard conditions with the measurements of the proportions of the isomerides formed remains unimpaired by the slight differences in medium in the two sets of experiments, since the latter values are but little affected by large variations in the medium.

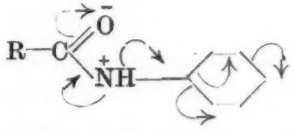
TABLE IV.

Chlorination in 99% acetic acid at 20°.

Molar proportions of HCl added :—	1·5	5	10	20
k for :				
Formanilide	8·9	9·2	—	10·2
Acetanilide	66·5	62·2	59·6	55·7
Benzanilide	—	69·1	—	—
Benzenesulphonanilide	41·5	42·7	44·4	46·9

Discussion of Results.

The bearing of modern theories on the rates of entrance of chlorine into a given position, either ortho or para, for the different anilides may be briefly examined. According to Allan, Oxford, R. Robinson, and Smith (J., 1926, 403) and Ingold and Ingold (*ibid.*, p. 1311), the directing influence of the acylamido-group is to be attributed to the tendency of the nitrogen atom to act as an electron source, as modified by a betaine-like electronic conjugation with the oxygen of the carbonyl group :



Both these processes result in the acquirement of a positive charge by the nitrogen atom. The tendency for the nitrogen to act as an

electron source towards the nucleus is said to be the greater the more negative (or less positive) it is originally.

The process I (below) is exactly analogous to the process leading to the ionisation of the corresponding carboxylic acid (Allan, Oxford, Robinson, and Smith, *loc. cit.*, p. 405; Lea and Robinson, *ibid.*, p. 2352), so that whatever effect R may have on (II) should also be manifest to a greater or lesser extent in (I), that is, the greater the

strength of the acid (II) the greater the tendency of the nitrogen in (I) to acquire a positive charge by this process, and hence the lesser tendency of the nitrogen atom to act as an electron source toward the nucleus. Hence the directing effect of the group R·CO·NH· should decrease with increase in the ionisation constant of the acid $R{\cdot}CO_2H$.

According to Allan, Oxford, Robinson, and Smith (*loc. cit.*, p. 407), in comparing the directive powers of groups it may be considered that what is being compared is the number of occasions in unit time that effectual polarisations take place, *i.e.*, the velocity of substitution at a given carbon atom is the measure of the directive power of a group. In the present case, since the different acyl groups do not alter the proportions of the isomerides appreciably, the velocity coefficients given in Table III, column 1, may be taken directly as a comparative measure of the directing effects of the groups concerned on either the ortho- or the para-position. These are seen to be in the order $C_6H_5{\cdot}CO{\cdot}NH{-}>CH_3{\cdot}CO{\cdot}NH{-}>H{\cdot}CO{\cdot}NH{-}$, whereas from the foregoing theoretical considerations the order should be $CH_3{\cdot}CO{\cdot}NH{-}>C_6H_5{\cdot}CO{\cdot}NH{-}>H{\cdot}CO{\cdot}NH{-}$.

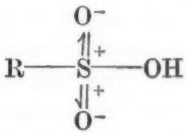
If it be assumed, as would appear to be reasonable, that the proportions of the isomerides formed by the chlorination of propionanilide, butyranilide, and *iso*valeranilide are not very different from those formed by the chlorination of acetanilide, the velocity coefficients obtained by Orton and King lead to the series :

$$C_2H_5{\cdot}CO{\cdot}NH{-}>\begin{matrix}C_3H_7{\cdot}CO{\cdot}NH{-}\\C_4H_9{\cdot}CO{\cdot}NH{-}\end{matrix}>C_6H_5{\cdot}CO{\cdot}NH{-}>$$
$$CH_3{\cdot}CO{\cdot}NH{-}>H{\cdot}CO{\cdot}NH{-}$$

corresponding with the theoretical sequence, except that again the group $C_6H_5{\cdot}CO{\cdot}NH{-}$ should follow $CH_3{\cdot}CO{\cdot}NH{-}$, instead of preceding it.

The benzenesulphonamido-group requires special consideration, since here no betaine-like process of electronic conjugation takes

place. The ionisation of a sulphonic acid may be attributed to the effect of the positive charges on the sulphur atom, which tend to loosen the binding between the hydroxyl oxygen and the hydrogen atom,



In a similar way, the nitrogen atom of a sulphonanilide is rendered somewhat positive, and although perhaps it is not justifiable to compare the effect of the sulphonyl group with that of a carboxyl group, since a different mechanism is called into play, from the consideration of the strength of a sulphonic acid, it is rather surprising to find the benzenesulphonamido-group nearly as strongly directing as the acetamido-group.

On an alternative view, the ionisation of a sulphonic acid may be attributed to the tendency of a sulphur atom to act as the positive end of a semipolar bond, a tendency which is satisfied in its higher valency states. Hence we have in a sulphonic acid, and in a sulphonamide, the tendency towards the following :

a tendency which, with the sulphonamide, is fulfilled when salt formation takes place (compare Clarke, Kenyon, and Phillips, J., 1927, 188). In the sulphonanilide, then, the nitrogen atom is tending to become negative, but forming a dipole arrangement (Goss, Ingold, and Wilson, J., 1926, 2440; Baker and Ingold, *ibid.*, p. 2462) with the proton. Although it is difficult to foresee the extent to which this dipole arrangement affects the tendency of the group to act as an electron source towards the nucleus, nevertheless this view appears more in harmony with the fact that the rate of chlorination of benzenesulphonanilide is more rapid than that of formanilide.

An extension of this investigation to other compounds containing the groups $-NRR$ and $-OR$ is in progress.

Experimental.

Analysis of Mixtures of o- *and* p-*Chloroacetanilides.—Melting-point method.* The melting point of the chlorination product of acetanilide was determined by the method described by G. Owen (J., 1923, **123**, 3394) and the composition read off from a curve

constructed from the data given by Orton and G. Owen (J., 1924, **125**, 766) for the melting points of mixtures of *o*- and *p*-chloroacetanilides. In some of the earlier experiments the eutectic point was determined, after the addition of a known quantity of the ortho-compound to bring the composition of the mixture to the region where the eutectic point could be realised, to demonstrate the absence of a third substance. The method, however, lacks accuracy, and was not employed after the development of the sublimation method of obtaining an independent check on the composition of the chlorination product.

Sublimation method. The difference between the vapour pressures of *o*- and *p*-chloroacetanilides (Sidgwick and Rubie, J., 1921, **119**, 1013) would suggest that at least a partial separation of the isomerides could be obtained by sublimation. It is found that the separation is quantitative when the sublimation is carried out in the following way. The finely powdered mixture of *o*- and *p*-chloroacetanilides is spread in a thin layer on a watch glass which is placed on the top of an air-oven, and a wide funnel clamped over it in an inverted position so that the edge of the funnel just clears the watch glass.

The internal temperature of the oven is maintained at 110°, the temperature of the solid on the watch glass probably being about 50—60°. The *o*-chloroacetanilide sublimes and condenses to some extent on the sides of the funnel, although part escapes through the stem (dimensions of funnel employed : width 10 cm., length 17 cm.). The watch glass and contents are weighed from time to time, and after 12—15 hours' heating are at a constant weight. In a control experiment, a mixture containing 62·4% of *p*-chloroacetanilide gave, by this method, (*a*) 62·3%, (*b*) 61·8% of the para-compound. The residual solid melted sharply at 178°, and was therefore completely free from the ortho-compound. The presence in the mixture to be analysed of any *m*-chloroacetanilide, which is non-volatile under these conditions, shows itself by the lowering of the melting point of the solid remaining, whilst unchanged acetanilide or 2 : 4-dichloroacetanilide volatilises so slowly that when 3—4% is present a constant weight is not attained even after 36 hours' heating. In no case did the sublimation method of analysis give any indication of a third substance in the chlorination products here described.

Method of Chlorination.—The selection of a chloroamine for use as a source of chlorine (Orton and King, *loc. cit.*) is in the present case guided by the following considerations : (1) The chloroamine must be stable, and readily obtained in a state of purity, (2) a quantitative separation of the parent substance from the chlorinated product must be possible. Two chloroamines fulfil these requirements, chloroacetamide, the acetamide being readily soluble in water,

and *p*-toluenesulphondichloroamide, "dichloramine T," the sulphonamide being readily soluble in alkali, whilst the chloroanilides are almost insoluble in water or alkali.

Dichloramine T was prepared as follows (compare Chattaway, J., 1905, **87**, 145; Kraus and Crede, *J. Amer. Chem. Soc.*, 1917, **39**, 2720). 10 G. of *p*-toluenesulphonamide are dissolved in 100 c.c. of acetic acid, and 120 c.c. of a 2·5*N*-solution of bleaching powder slowly run in with shaking and cooling. The fine crystalline powder is collected, and without drying dissolved in 75 c.c. of hot acetic acid, and reprecipitated by the addition of 37 c.c. of *N*/10-bleaching powder solution. Yield, 15 g. (Found: Cl, by titration, 29·43. Calc.: Cl, 29·53%).

Preparation of Chloroacetamide (compare Hofmann, *Ber.*, 1882, **15**, 407; Hantzsch and Dollfuss, *Ber.*, 1902, **35**, 252; Mauguin, *Ann. Chim. Phys.*, 1911, **22**, 297; Boismenu, *Compt. rend.*, 1911, **153**, 1482).—A good yield is obtained by dissolving 35 g. of acetamide in 80 c.c. of water, and adding 50 g. of sodium bicarbonate. A fairly rapid current of chlorine is led in, the solution being kept cool. After a time, the bulky mass of chloroacetamide and sodium chloride is filtered off, and after the addition of a further quantity of sodium bicarbonate to the filtrate the passage of chlorine is continued. The combined solid products are dried and extracted with warm chloroform, the sodium chloride is filtered off, and on cooling, the chloroacetamide separates. Yield, 34 g. (Found: Cl, by titration, 38·01. Calc.: Cl, 37·97%).

Chlorination of Acetanilide in Chloroform.—The chloroform used was washed with water, kept over lime, and filtered before use. In early experiments, about 10 g. of acetanilide together with the requisite quantity of chloroacetamide were dissolved in chloroform, and about 1/10 molar proportion of hydrochloric acid was added. When chlorination was complete, as indicated by titration, the chloroform was removed by distillation and the residue extracted with a small quantity of water. The solid so obtained melted to a dark-coloured liquid and rapidly became dark-coloured in air, and it would appear that some by-product, presumably an oxidation product, is formed during chlorination. The following process, involving a purification of the crude product, was therefore adopted. 2·7 G. (1 mol.) of acetanilide and 2·4 g. of dichloramine T (0·5 mol.) were dissolved in 50 c.c. of chloroform and placed in a thermostat at 20°, hydrochloric acid (0·09 mol.) being added in the form of a concentrated aqueous solution. After 5 hours, chlorination was complete and the chloroform was removed by distillation. The solid residue in the flask was boiled under reflux with 50 c.c. of 10% sulphuric acid for 2 hours, the whole dissolving to a straw-coloured

solution, which was made alkaline and distilled in steam. The anilines passing over were collected with chloroform and acetylated by the addition of acetic anhydride to the chloroform solution, the chloroform being allowed to boil away during the acetylation. The excess acetic anhydride and acetic acid formed were removed in a vacuum desiccator over sodium hydroxide. That this method of purification and isolation effects no noteworthy alteration in the proportion of the isomerides is shown by a control experiment, in which a mixture of *o*- and *p*-chloroacetanilides, m. p. 149·7°, after being put through the complete process melted at 149·2°.

The yield and analytical data for duplicate experiments are appended.

(*a*) Yield 96·8%, m. p. 157·7° = 69·5% para. Eutectic point 76·6°, from curve 77°. Sublimation gave 68·3%, 68·1% para.

(*b*) Yield 93·2%, m. p. 156·4° = 68% para. Eutectic point 77°. Sublimation gave 67·4%, 67·4% para.

Chlorination in Acetic Acid.—The acetic acid used, after purification as described by Orton and Bradfield (J., 1924, **125**, 960), melted at 16°. After chlorination with dichloramine T in a manner exactly similar to that described above, the acetic acid was removed by distillation under 11 mm. pressure. The product was hydrolysed, distilled in steam, etc., as before.

(*a*) Yield 92%, m. p. 156·5° = 68% para. Sublimation gave 67·5%, 67·5% para.

(*b*) Yield 91%, m. p. 156·0° = 67·3% para. Sublimation gave 67·0%, 67·0% para.

Chlorination in 50% *Acetic Acid.*—As dichloramine T is only slightly soluble in 50% acetic acid, the use of a large bulk of liquid is avoided by the following procedure. 2·7 G. of acetanilide (1 mol.) were dissolved in 50 c.c. of 50% acetic acid, to which 0·09 mol. of concentrated hydrochloric acid was added, and placed in a bath at 20°. The calculated quantity of a solution of dichloramine T in glacial acetic acid was run in in small portions, simultaneous addition of water keeping the medium as nearly 50% as possible. The solution was evaporated to dryness under a pressure of 11 mm., and the product worked up as before.

(*a*) Yield 93·8%, m. p. 150·6° = 60·7% para. Sublimation gave 61·3%, 61·2% para.

(*b*) Yield 90·6%, m. p. 150·4° = 60·5% para. Sublimation gave 60·5% para.

Chlorination in Methyl Alcohol.—Methyl alcohol "free from acetone" is only slowly attacked by chlorine. Nevertheless, for the chlorination, which was carried out in the usual way, a 5% excess of dichloramine T was taken to compensate for that lost by reaction

with the medium. When chlorination was complete, the methyl alcohol was distilled off under diminished pressure, and the product hydrolysed, etc., as before.

(*a*) Yield 89%, m. p. 150·2° = 60·2% para. Sublimation gave 61·2%, 61·1% para.

(*b*) Yield 91%, m. p. 150·5° = 60·5% para. Sublimation gave 60·5%, 60·6% para.

Transformation of N-*Chloroacetanilide.*—*N*-Chloroacetanilide was prepared by the method described by Chattaway and Orton (J., 1899, **75**, 1046), and the transformation effected in the various solvents by the addition of 1/10 molar proportion of hydrochloric acid, in a manner completely analogous to the chlorination experiments described above. The isolation of the product was also carried out in the same way. Analytical data :

Transformation of N-*chloroacetanilide in chloroform.* (*a*) Yield 90%, m. p. 158·0° = 69·8% para. Sublimation gave 69·9%, 69·6% para.

(*b*) Yield 89%, m. p. 157·8° = 69·6% para. Sublimation gave 70·0%, 70·0% para.

Transformation of N-*chloroacetanilide in acetic acid.* (*a*) Yield 89%, m. p. 155·7° = 67% para. Sublimation gave 67·5%, 67·5% para.

(*b*) Yield 89%, m. p. 155·0° = 66·0% para. Sublimation gave 66·4%, 66·7% para.

Transformation of N-*chloroacetanilide in* 50% *acetic acid.* (*a*) Yield 92·3%, m. p. 146·9° = 56·9% para. Sublimation gave 57·8%, 57·8% para.

(*b*) Yield 92·9%, m. p. 146·6° = 56·6% para. Sublimation gave 57·6%, 57·8% para.

Chlorination of Formanilide in Acetic Acid.—2·42 G. (1 mol.) of formanilide, m. p. 48°, and 2·4 g. (0·5 mol.) of dichloramine T were dissolved in 50 c.c. of acetic acid, maintained at 20°, and hydrochloric acid (0·09 mol.) was added. The acetic acid was removed under diminished pressure. The product was hydrolysed with a mixture of equal volumes of concentrated sulphuric acid and water, and the anilines were distilled in steam, collected as for acetanilide, and acetylated for analysis.

(*a*) Yield 84%, m. p. 157·5° = 69·2% para. Sublimation gave 69·4%, 69·7% para.

(*b*) Yield 85%, m. p. 158·0° = 69·9% para. Sublimation gave 71·0%, 70·9% para.

Chlorination of Benzanilide in Acetic Acid.—Benzanilide, m. p. 162°, requires 200 c.c. of acetic acid to dissolve 3·94 g. Chlorination was effected in the above-described manner, the product hydrolysed with a mixture of 1 volume of concentrated sulphuric acid and 2

volumes of water, and the anilines were distilled in steam and acetylated for analysis.

(*a*) Yield 92%, m. p. 157·9° = 69·7% para. Sublimation gave 68·8%, 68·7% para.

(*b*) Yield 92%, m. p. 158·7° = 70·7% para. Sublimation gave 69·4%, 69·6% para.

Chlorination of Benzenesulphonanilide in Acetic Acid.—The chlorination of benzenesulphonanilide, m. p. 110°, was carried out in the usual way. Sulphuric acid of 60% strength is needed for the hydrolysis of the chloroanilides. The anilines obtained were acetylated for analysis.

(*a*) Yield 86·4%, m. p. 154° = 65% para. Sublimation gave 64·3%, 64·3% para.

(*b*) Yield 90%, m. p. 154·4° = 65·4% para. Sublimation gave 65·5%, 65·4% para.

Velocity Determinations.—The determination of the velocity of chlorination of the anilides was carried out by the method described by Orton and King (*loc. cit.*), who used *N* : 2 : 4-trichloroacetanilide as a source of chlorine. This chloroamine and dichloramine T were both used in the experiments now described, the same values for the coefficients being obtained whichever chloroamine was employed.

The anilide was dissolved in 40—50 c.c. of acetic acid, m. p. 16·2—16·4°, prepared as described by Orton and Bradfield (this vol., p. 983), in a 100 c.c. flask, and the required quantity of a freshly standardised solution of the chloroamine run in. The amount of water which, together with the water present in the acetic acid and that to be added with the hydrochloric acid (of which a constant-boiling solution was used), would make up 1 c.c. was added, and the solution made up with acetic acid nearly to the 100 c.c. mark. When the solution had attained the temperature of the thermostat, 20° $\pm$ 0·05°, the necessary amount of hydrochloric acid was added, the contents of the flask rapidly mixed by shaking, and the flask replaced in the thermostat. 10 C.c. were removed at intervals and run into potassium iodide solution, the time of half delivery of the pipette, which could be estimated to $\pm$ 2 sec., was noted, and the liberated iodine titrated with *N*/100-thiosulphate, with the usual precautions to secure a good end-point.

The loss of chlorine to the vapour phase, consequent upon increasing the air space in the flask, has an appreciable effect if more than three or four portions are removed in any one experiment, so that in these experiments measurements were limited to a few titres during the middle period of the reaction (35%—65% change). Further, since the object in view is to obtain figures which shall represent the relative speeds of chlorination under standard con-

ditions, rather than to establish the true bimolecular nature of the reaction, measurements were only made with anilide and chlorine at the same initial concentration, which was 0·0025 mol./litre in every case.

The velocity coefficient, k, was calculated from the expression $k = x/at(a - x)$, the time being expressed in minutes. The values given above (Table IV) represent the mean values for at least two concordant experiments. As an example of the constancy of k in any one experiment, the following is quoted as typical:

Chlorination of benzenesulphonanilide.

a = 0·0025 mol./litre. HCl = 0·00375 mol./litre.

Time (±0·03 min.).	% changed.	k.
7·02	39·6	40·8
13·28	57·9	41·4
16·97	63·7	41·3
	Mean	41·2

The reproducibility of the values is shown by the following data for the velocity measurements for acetanilide:

Chlorination of acetanilide.

Molar proportions of HCl.	Mean values of k for individual experiments.	Mean k.
1·5	67·0, 66·0	66·5
5	62·8, 60·9, 62·8	62·2
10	59·5, 60·4, 57·9, 60·0, 60·2	59·6
20	55·6, 55·8	55·7

One of us (A. E. B.) wishes to express his thanks to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant.

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BANGOR.

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CXXXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part XVIII. Mechanism of Exhaustive Methylation and its Relation to Anomalous Hydrolysis.*

By WALTHER HANHART and CHRISTOPHER KELK INGOLD.

THE decomposition of quaternary ammonium compounds has been extensively investigated and often exploited for the synthesis of olefins and the degradation of complex bases; nevertheless, no general theory of the mechanism of the process seems to have been advanced. Unquestionably the facts to be explained are numerous

and complex; in particular, a satisfactory theory should embrace the following points:

(1) The hydrogen atom eliminated along with hydroxyl in the reaction $R{\cdot}CH_2{\cdot}CH_2{\cdot}NR'_3{\cdot}OH = R{\cdot}CH{:}CH_2 + NR'_3 + H_2O$ is apparently one of those attached to the second carbon atom from the nitrogen atom. Assuming that this is definitely the case (below), then, since one can hardly suppose otherwise than that the cause of molecular instability originates in the ammonium group, it must be explained, first, how the necessary reactivity is propagated to such a distant hydrogen atom through two intervening *saturated* carbon atoms without imparting *en route* a still greater reactivity to the hydrogen atoms attached to the first carbon atom, and, secondly, why the transmitted effect emerges just where it does.

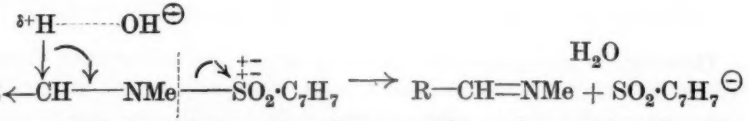
(2) When the four alkyl groups attached to the nitrogen atom are such that different olefins might be produced by decomposition in different directions, the one actually formed has always been found to be ethylene if an ethyl group is present. It is shown below that this generalisation, sometimes referred to as Hofmann's rule, is subject to certain exceptions: the reasons for the rule and the causes of the exceptions both require elucidation.

(3) The synthesis of olefins from quaternary ammonium hydroxides sometimes fails owing to the elimination of an alcohol: $R^1R^2R^3R^4N{\cdot}OH = R^1R^2R^3N + R^4{\cdot}OH$. It is desirable to be able to foretell when and to what extent this is likely to take place.

(4) Quaternary ammonium salts (*e.g.*, chlorides) often decompose differently from the hydroxides. In certain cases both chlorides and hydroxides give corresponding products, but where a difference exists it is the hydroxide which yields the olefin and the salt which gives the alkyl halide or ester. Moreover, the chloride usually decomposes less easily than the corresponding hydroxide. Since both are strong electrolytes and the organic ion is the same in each, these differences of reactivity and their lack of complete uniformity both require explanation.

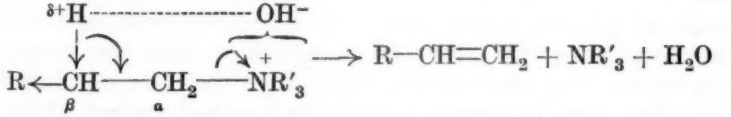
The hypothesis which, we believe, suffices to interpret all these phenomena was outlined in Part IV (J., 1926, 1305) in connexion with hydrolysis, and may be expressed in general terms as follows: Hydrogen atoms in organic molecules, even those in hydrocarbon radicals, exist to a greater or less degree in a condition of incipient ionisation depending on the electron-affinity of the surrounding groups, $\leftarrow\!\!-C\leftarrow\!\!-H(\delta+)$; when a hydrogen atom is abstracted as hydrion by a reagent having sufficient proton-affinity to effect its removal in this form, the electrons which held it become absorbed into the residue of the molecule in a manner which again

is determined by the electron-affinity of the groups present. The proton-affinity of a reagent is measured by the electrolytic dissociation of its compound with a hydrogen ion; thus the hydroxide ion must have a large proton-affinity, since water is scarcely dissociated. The electron-affinities of groups may be inferred from their influence on the strengths of acids and bases (Lewis), their effect on the mobility of tautomeric systems (Ingold, Shoppee, and Thorpe, J., 1926, 1427), their orienting action in additions (Lucas and Moyse, *J. Amer. Chem. Soc.*, 1925, **47**, 1459) and substitutions (compare *Ann. Reports*, 1926, 129), and their effect on the dipole moments of molecules (compare *loc. cit.*). The hypothesis was tested in Part IV through the theoretical deduction that sulphonamides on *alkaline* hydrolysis ought to yield, not the normal sulphonic acid and amine, but a sulphinic acid (*i.e.*, sulphinate ion) and an imine, provided that the electron-affinity of R is sufficient.



A consideration of the strengths as acids or bases of such compounds as phenol and aniline suggests that the phenyl group can exert a moderate electron-attraction, and in the case $R = C_6H_5$ the above anomalous mode of hydrolysis was realised. The direction of the disruption in this and all similar cases is determined by the circumstance that, as the hydroxide ion draws off the proton, so the electrons relieved from its attraction move towards the positively charged (sulphur) atom.

The application to the decomposition of quaternary ammonium hydroxides is obvious: the positive pole to which the liberated electrons move is the ammonium nitrogen atom, and it is unnecessary to add an alkali because the compound contains its own hydroxide ions:



We may now consider how this hypothesis applies to the four points mentioned at the outset.*

* It is not attempted to distinguish between the possible variations of the general mechanism, *e.g.*, possible lack of complete synchronisation of the electron transfers. The intention is to present only a preliminary survey of the field; each of the aspects thus outlined will be made the subject of a future, more detailed communication.

(1) The only alternative to the view that a β-hydrogen atom enters into the constitution of the eliminated water molecule is that one of the α-hydrogen atoms is first removed, the bivalent-carbon compound (sextet) so formed undergoing rearrangement:

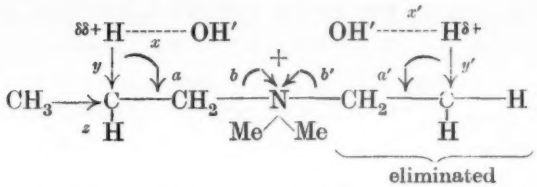
$$\{CH_3{\cdot}CH_2{\cdot}NR_3\}^{\cdot}\,OH' \longrightarrow CH_3{\cdot}CH{:} \longrightarrow CH_2{:}CH_2$$

There are many arguments against this theory; *e.g.*, ethylene has never been detected amongst the decomposition products of tetramethylammonium hydroxide, nor has stilbene been obtained from benzyltrimethylammonium hydroxide; yet these products would be expected to appear if a bivalent carbon compound intervened. Positive evidence against the rearrangement theory is provided by the observation that alkyltrimethylammonium hydroxides, which have no α-hydrogen atoms, decompose in the normal manner (Kohn, Schlegl, and Morgenstern, *Monatsh.*, 1907, **28**, 491, 525; compare p. 1004):

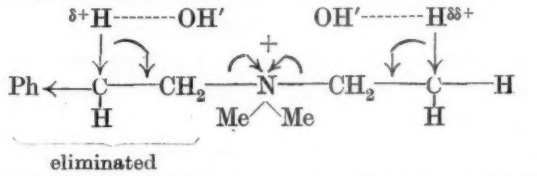
$$\{R{\cdot}CH_2{\cdot}CMe_2{\cdot}NMe_3\}^{\cdot}\,OH' \longrightarrow R{\cdot}CH{:}CMe_2 + NMe_3 + H_2O$$

Therefore it seems certain that it is one of the β-hydrogen atoms which is originally eliminated; and the mechanism suggested necessitates the direct abstraction of this hydrogen atom, since the removal of no other would enable the mutually accommodating *integral* electron displacements to occur with preservation of the octets.

(2) The rule that ethylene is eliminated in preference to any higher unsaturated hydrocarbon in quaternary ammonium hydroxide distillations is one to which we cannot call to mind any recorded exception. It is true that, as in Hofmann's original instances, *e.g.*, amyltriethylammonium hydroxide, most of the examples by which the rule has been illustrated are affected by the circumstance that several ethyl groups were present in the ammonium compound, which might therefore be predisposed to eliminate ethylene owing to statistical factors. This is not so, however, in the case of *dimethylethyl*-n-*propylammonium hydroxide*, which, as we have found, also yields mainly ethylene, and only a very little propylene. This is in agreement with the foregoing hypothesis; for, since alkyl groups repel their shared electrons more than does hydrogen (Lucas), the terminal methyl group of the propyl chain will reduce (z) the incipient ionisation (y) of the propyl β-hydrogen atom below that (y') of the ethyl β-hydrogen atom. That is to say, the extraction of the propyl proton by a hydroxide ion (x, y), and the dependent decomposition (a, b), will be hindered relatively to the extraction of the ethyl proton (x', y') and its dependent decomposition (a', b'):



Similarly, it follows that dimethyl-*n*-propyl-*n*-butylammonium hydroxide should yield more propylene than butylene, that dimethyl-*n*-butyl-*iso*butylammonium hydroxide should give *n*-butylene, and not *iso*butylene, as the main olefinic product; many similar predictions may be made; it is also clear that the only reason why no exception has previously been found to the Hofmann rule is that the groups with which ethyl has been placed in competition have hitherto all been of one type, namely, $-CH_2{\cdot}CH_2R$ or $-CH_2{\cdot}CHR_2$, where R has a smaller electron-affinity than hydrogen. Hence, if R were phenyl, the rule should be disobeyed—a deduction we have tested and found correct:



Again, a β-*p*-nitrophenylethyl group should be more readily eliminated as olefin than an unsubstituted β-phenylethyl group, and this also we have verified.

Thus it is possible to construct a series representing the relative ease of elimination of groups as olefins, and the sequence established by the above experiments,

$$CH_3{\cdot}CH_2{\cdot}CH_2 < H{\cdot}CH_2{\cdot}CH_2 < C_6H_5{\cdot}CH_2{\cdot}CH_2 < NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2,$$

could, of course, be filled in with many other groups from theoretical considerations. It should also be emphasised that such a series indicates not only the direction of a particular decomposition, but also the ease with which it will take place. Thus we found that decompositions resulting in the elimination of propylene or ethylene always required a fairly high temperature, whereas that which gave styrene occurred in hot dilute aqueous solution, and that which yielded *p*-nitrostyrene took place during the attempted preparation of the quaternary compound, which we were unable to isolate for this reason.

One more example may be given. From the probable increasing electron-affinity of the groups in the series CH_3, NH_2, OH, Cl—as indicated, for example, by the increasing proportion of *m*-substi-

tution in $CH_3{\cdot}COPh$, $NH_2{\cdot}COPh$, $OH{\cdot}COPh$, $Cl{\cdot}COPh$ (Cooper and Ingold, this vol., p. 836)—it follows that the ammonium hydroxides

$$CH_3{\cdot}C_2H_4{\cdot}C_2H_5{>}\overset{OH}{\widetilde{NMe_2}}, \quad NH_2{\cdot}C_2H_4{\cdot}C_2H_5{>}\overset{OH}{\widetilde{NMe_2}}, \quad OH{\cdot}C_2H_4{\cdot}C_2H_5{>}\overset{OH}{\widetilde{NMe_2}},$$

$$Cl{\cdot}C_2H_4{\cdot}C_2H_5{>}\overset{OH}{\widetilde{NMe_2}},$$

should yield successively diminishing proportions of ethylene and increasing proportions of dimethylethylamine on decomposition. This appears to be the case. The main products obtained from the first compound are ethylene and dimethylpropylamine; the second gives corresponding principal products ethylene and β-aminoethyldimethylamine, but in addition yields acetaldehyde (evidently derived from vinylamine) and an appreciable quantity of dimethylethylamine; the third compound of the series yields still less ethylene, and appears to give more acetaldehyde (vinyl alcohol), and nearly equal amounts of dimethylethylamine and β-hydroxyethyldimethylamine; finally, the chloro-compound yields no appreciable quantity of ethylene, but gives a basic product consisting mainly of dimethylethylamine—another exception to Hofmann's rule.

It will be evident from these examples that the decomposition of quaternary ammonium hydroxides furnishes a means of comparing electron-affinities which should be capable of many applications.

(3) In the above examples, the ammonium atom achieves neutrality by the appropriation of electrons which become available as a direct consequence of the withdrawal of a β-hydrion from one of the alkyl groups. It may happen, however, (i) that this mechanism cannot function owing to the absence of β-hydrogen atoms, (ii) that it either cannot function, or can do so only with great difficulty, owing to the more or less effective stabilisation of all the existing β-protons by the strong electron-repulsion of neighbouring groups. In these cases, the only other means open to the nitrogen atom is to extract the shared electrons from a group without the independent facilitation of a compensating supply of electrons for the depleted carbon atom; in this event, the group is ejected as a positive ion, which will at once unite with any negative ion that happens to be present in the liquid, so that in the decompositions now under consideration it appears as an alcohol (compare following section):

$$R'R''R'''\overset{+}{N}\!\!\curvearrowleft\!\!—R + \bar{O}H = R'R''R'''N + \overset{+}{R} + \bar{O}H = R'R''R'''N + R{\cdot}OH.$$

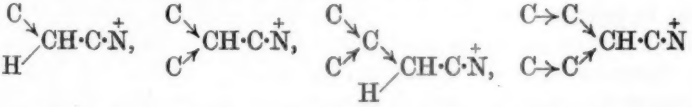
Which of the four groups will thus be eliminated, and the facility of the process, will depend on the relative stabilities of the possible positive ions, and these in turn can be inferred, for example, from the reactivities of the iodides RI, R′I, R″I, R‴I towards the same ionising substance. Thus, amongst the commoner groups devoid of an available β-hydrogen atom the order of ease of elimination should be $Ph_3C>Ph_2CH>PhCH_2>CH_3>Ph$, and this has been confirmed for the last three groups by Collie and Schryver (J., 1890, **57**, 767), who found that benzyltrimethylammonium hydroxide yielded benzyl alcohol, whilst phenyltrimethylammonium hydroxide gave methyl alcohol on distillation.

In considering the relative ease of elimination of any *one* group as alcohol from various ammonium hydroxides which can also yield an olefin, we may take for illustration the elimination of methyl alcohol, since this is the case which usually arises in exhaustive methylations. If the quaternary hydroxide is of the form $\{AlkNMe_3\}\cdot OH'$, the possible decompositions are:

$$\left.\begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!CH\!-\!\overset{R^3}{\underset{R^4}{C}}\!-\!\overset{+}{N}Me_3\right\}\bar{O}H \rightarrow \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!C\!::\!C\!<\!\begin{matrix} R^3 \\ R^4 \end{matrix} + NMe_3 + H_2O \quad . \quad (A)$$

$$\rightarrow \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!CH\cdot CR^3R^4\cdot NMe_2 + MeOH \, . \quad (B)$$

Now since (B) takes place only when (A) is inhibited, it follows that the occurrence of (B) depends primarily on the electron-repulsion of R^1 and R^2; it will depend only to a small extent on the groups R^3 and R^4, because any electronic strain set up by these radicals can reach the β-hydrogen atom only indirectly. From a consideration of strain-paths such as



it can be seen that the order of the effects due to alkyl groups R^1 and R^2 should be: $CH_3\cdot[CH_2]_n>CH_3\cdot[CH_2]_{n-1}>\ldots\ldots>CH_3>H$; and $(CH_3)_2>CH_3\cdot CH_2$, $(CH_3)_2CH>CH_3\cdot[CH_2]_2$, etc.; or, in words, longer chains should be more effective than shorter, and branched chains more effective than isomeric normal chains. Also it would be expected that the effect of the more remote parts of long chains would be small in comparison with that of the portions nearer the β-hydrogen atom.

The following table shows how far these conclusions are supported by experimental data relating to the effect of alkyl groups on the elimination of methyl alcohol from hydroxides of the type $\{AlkNMe_3\}\cdot OH'$.

Decomposition of Trimethylalkylammonium Hydroxides.

No.	Alkyl group.	R^1.	R^2.	R^3.	R^4.	Reaction B (%).
1	Ethyl.	H	H	H	H	0
2	*iso*Propyl.	H	H	CH_3	H	0
3	*sec.*-Butyl.	H	H	$CH_3 \cdot CH_2$	H	Small.
4	*sec.*-Amyl.	H	H	$CH_3 \cdot CH_2 \cdot CH_2$	H	Small.
5	*tert.*-Butyl.	H	H	CH_3	CH_3	Small.
6	*n*-Propyl.	CH_3	H	H	H	19
7	*n*-Butyl.	$CH_3 \cdot CH_2$	H	H	H	25
8	*iso*Butyl	CH_3	CH_3	H	H	37
9	*β*-Ethyl-*n*-butyl.	$CH_3 \cdot CH_2$	$CH_3 \cdot CH_2$	H	H	57
10	*β*-*n*-Propyl-*n*-amyl.	$CH_3 \cdot CH_2 \cdot CH_2$	$CH_3 \cdot CH_2 \cdot CH_2$	H	H	69

The figures for examples (1) and (2) are taken from Collie and Schryver's published results; the experimental basis for the remainder is recorded in this paper, but example (6) was investigated also by Collie and Schryver, whose observations accord with the figure given. In addition to these results, data have been recorded by von Braun (*Annalen*, 1911, **382**, 1) which appear to establish the anticipated sequence of alkyl groups:

n-Butyl<*n*-Amyl<*n*-Hexyl<*n*-Heptyl, *n*-Octyl, ... *n*-Cetyl

but these are not included in the table, because, although they are in the correct order relatively, we doubt their essential accuracy: certainly, von Braun's results for trimethyl-*n*-butylammonium hydroxide differ widely from ours, and it is proposed to reinvestigate the other cases. In the meantime it is quite clear (i) that β-alkyl substituents (R^1, R^2) are more effective than α-alkyl groups (R^3, R^4) in promoting reaction B, (ii) that the rule for normal chains holds at least for the lower members: $H < CH_3 < C_2H_5 < C_3H_7$, and (iii) that a comparison of the *n*- and *iso*butyl-compounds exemplifies the predicted effect due to the branching of carbon chains.

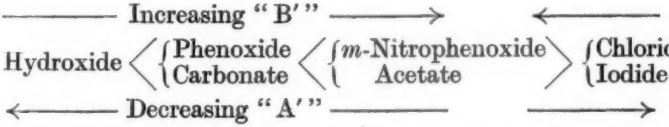
(4) It follows from the basic hypothesis that the ease of removal of the β-proton (reaction A) depends (*a*) on its vulnerability, (*b*) on the proton-avidity of the attacking anion. Factor (*a*) has been discussed (Section 3); now it is necessary to consider factor (*b*).

In order to maintain factor (*a*) constant, we must consider a *single* ammonium ion, and the example chosen for experimental study was No. 6 in the table. Now a precise measure of the proton-affinity of an attacking anion X′ would be available if the electrolytic dissociation constant of the compound $HX(\rightleftharpoons H^{\cdot} + X')$ under the conditions of the decomposition (*i.e.*, in the fused material) were known. Such data, however, are not available, and in their absence the most acceptable criterion is the dissociation constant in water or some other solvent. Adopting this view, and remembering that it may possibly lead to anomalies, since the relative strengths of electrolytes are known to be sometimes inverted on passing from non-aqueous solvents to water, it follows that reaction (A′) might

be successively inhibited and (B′) correspondingly favoured on passing through such a series as the quaternary hydroxide, phenoxide, nitrophenoxide, chloride; thus, since the hydroxide gives 19% of methyl alcohol, the phenoxide should yield a greater proportion of anisole, and a nitrophenoxide still more nitroanisole, for phenol is a stronger acid than water, and the nitrophenols are stronger than phenol.

$$C_3H_7\cdot\overset{+}{N}Me_3\}\ \bar{X} \begin{cases} \nearrow C_3H_6 + NMe_3 + HX \quad . \quad . \quad . \quad (A') \\ \searrow C_3H_7\cdot NMe_2 + MeX \quad . \quad . \quad . \quad (B') \end{cases}$$

Actually our yields of anisole and *m*-nitroanisole were 65% and 89% respectively, and experiment establishes the following relationships amongst trimethyl-*n*-propylammonium hydroxide and six of its salts.



The first five substances are thus related in accordance with the tentative prediction based on aqueous acid-strengths, but the halogen salts are anomalous, since they give slightly more olefin than the nitrophenoxide or acetate. There is, however, nothing demonstrably inconsistent with the general theory in this behaviour, because the halogen acids are known to be almost wholly undissociated in most non-aqueous solvents, and it is not impossible that under the conditions of the decompositions hydrogen chloride and hydrogen iodide may be weaker acids than acetic acid.* The other conceivable source of disturbance, namely, the effect of the anions in directly facilitating the removal of the positive alkyl ions, we do not regard as likely to produce large irregularities, since, owing to the protection of the positive carbon nucleus by its surrounding shell of electrons, the direct attraction between that nucleus and any circumambient anions would presumably be relatively feeble.

Experimental.

(I). *Dimethylethyl-*n*-propylammonium Hydroxide.*—A modification of Eschweiler's method (*Ber.*, 1905, **38**, 881) was used for the preparation of dimethylethylamine. The solution obtained by neutralising 13·5 c.c. of 33% aqueous ethylamine with hydrochloric acid

* Hydrogen chloride is a non-conductor of electricity, but solutions of acetic acid in hydrogen chloride are good conductors (Archibald, *J. Amer. Chem. Soc.*, 1907, **29**, 1471).

was evaporated to a paste, which was then heated with 38% formaldehyde (20 c.c.) under pressure at 140—150° for 3—4 hours. The product of several such experiments was evaporated to a paste, which was treated with solid potassium hydroxide, the evolved bases, b. p. 30—40° (the greater part had b. p. 36°), being collected in well-cooled ether. The dimethylethylamine thus obtained was not pure, since it gave a non-crystalline quaternary iodide with *n*-propyl iodide. The tertiary base was therefore converted into its picrate with benzene–ethereal picric acid, and the salt crystallised from alcohol until its m. p. rose to and remained constant at 200—201°. The pure picrate was converted into the hydrochloride by shaking a suspension in hydrochloric acid with benzene; the free base, b. p. 36—38°, was then liberated.

The following method also was used. Well-dried ethylamine hydrochloride, prepared from 120 g. of 33% aqueous ethylamine, was thoroughly mixed with 90 g. of paraformaldehyde and heated under reflux for 2·5 hours at 135° (internal temperature). The product was covered with ether and decomposed with concentrated aqueous sodium hydroxide, and the ethereal solution of the base (it is undesirable to extract more than once with ether) was precipitated with ethereal picric acid (150 g.). The picrate was collected from the still warm suspension (the salt which subsequently separates being very impure), crystallised twice from water to remove a sparingly soluble oily product, converted into the hydrochloride and thence into the free base (yield, 25 g.).

A mixture of this (19 g.) with *n*-propyl iodide (50 g.) was kept for 4 days at the ordinary temperature, and the hygroscopic *dimethylethyl*-n-*propylammonium iodide* thus obtained was converted into the *picrate* by treatment with saturated aqueous sodium picrate. This salt separates from alcohol or water in orange-yellow needles or tablets, m. p. 185—187° (Found: C, 45·55; H, 6·0. $C_{13}H_{20}O_7N_4$ requires C, 45·35; H, 5·8%).

Decomposition of dimethylethyl-n-*propylammonium hydroxide.* A solution of this substance prepared from the iodide, silver oxide, and water was distilled through four wash-flasks. The first two contained 3*N*-hydrochloric acid, and the second two bromine, the first, third, and fourth being cooled in ice-water. Usually the decomposition products were completely trapped in the first and the third vessel.

Methyl alcohol was detected by distilling the hydrochloric acid solution and treating the first portion of the distillate with *p*-nitrobenzoyl chloride and alkali; a small amount of methyl *p*-nitrobenzoate, m. p. 92°, was then formed.

The olefin bromide, obtained after destruction of the excess of

bromine with freshly prepared sodium hydrogen sulphite, boiled completely at 131—132° (ethylene dibromide has b. p. 131°, propylene dibromide has b. p. 140°) and therefore consisted mainly of ethylene dibromide (Found: C, 13·2; H, 2·3%). The material was fractionally distilled, and analysis of the last few drops, b. p. about 132° (Found: C, 15·5, 15·2; H, 2·3, 2·35; Br, 82·1, 82·3. Calc. for $C_2H_4Br_2$: C, 12·8; H, 2·1; Br, 85·1. Calc. for $C_3H_6Br_2$: C, 17·8; H, 3·0; Br, 79·2%) showed that some propylene dibromide was present.

Confirmatory results were obtained on examining the basic decomposition products, which were first converted into their picrates. Analysis of the crude mixture indicated *dimethyl-n-propylammonium picrate* to be the principal constituent (Found: C, 41·9, 41·7; H, 4·9, 5·1. $C_{11}H_{16}O_7N_4$ requires C, 41·8; H, 5·1%), and 70% of this substance was readily isolated in stout, lemon-yellow prisms, m. p. 108—109°, by crystallisation from ethyl acetate (Found: C, 41·9; H, 5·4%). It was identified by conversion into trimethyl-*n*-propylammonium picrate, m. p. 195° (below). The residue was repeatedly fractionally crystallised from toluene and ethyl acetate, used for the most part alternately; besides a further quantity of dimethyl-*n*-propylammonium picrate, a small amount of dimethylethylammonium picrate (identified by mixed m. p.) was thus obtained, together with a residue which may have contained methylethylpropylammonium picrate, although we did not succeed in isolating this.

The hydroxide therefore decomposes mainly into dimethylpropylamine and ethylene, to a small extent into dimethylethylamine and propylene, and also to a slight extent into methyl alcohol and, presumably, methylethylpropylamine. This seems to be the first recorded instance of the formation of methyl alcohol in the decomposition of a quaternary ammonium hydroxide which also yields ethylene.

(II). *β-Phenylethyldimethylethylammonium Hydroxide.*—β-Phenylethyldimethylamine (Goss, Hanhart, and Ingold, this vol., p. 250) liberated from 28 g. of the picrate was warmed with a benzene solution of ethyl iodide (20 g.) for 2 hours on the water-bath. The *iodide* was collected (22 g.) and crystallised twice from alcohol–ethyl acetate; m. p. 158—159°. It is easily soluble in water, alcohol, and chloroform (Found: C, 47·5; H, 6·9. $C_{12}H_{20}NI$ requires C, 47·2; H, 6·6%).

The *picrate* appears to form two crystallographic modifications. The precipitate obtained by adding sodium picrate solution to an aqueous solution of the iodide melts at about 113°, and on crystallisation from alcohol forms well-defined, lemon-yellow needles, m. p.

96—97°. If, however, the needles are mixed with a trace of the crude product the m. p. is 115—116°, and if the melt obtained by heating the needles to just above 97° is treated with a "speck" of the crude powder, solidification at once occurs and the product then melts at 115—116°. The needles are only slightly soluble in cold ethyl alcohol, but are readily soluble in acetone (Found: C, 53·5; H, 5·6. $C_{18}H_{22}O_7N_4$ requires C, 53·2; H, 5·4%).

Decomposition of β-phenylethyldimethylethylammonium hydroxide. The aqueous solution of the hydroxide, prepared from the iodide and an aqueous suspension of silver oxide, began to decompose at 100°. The products were exclusively styrene and dimethylethylamine, both of which were isolated in the pure condition in excellent yield. The former, b. p. 140—143°, was characterised through its dibromide, m. p. 74°, which was compared with an authentic specimen. The latter was converted into its picrate, which formed large, lustrous, yellow leaves, m. p. 202—203° (not needle-like crystals, m. p. 193—194°, as described by Kohn and Morgenstern, *Monatsh.*, 1907, **28**, 496), and was identified by direct comparison and by analysis (Found: C, 40·0; H, 4·6. Calc.: C, 39·7; H, 4·6%).

In order to detect any decomposition in the direction leading to ethylene and β-phenylethyldimethylamine, a portion of the basic product was oxidised with permanganate under conditions in which this base yields benzoic acid quantitatively (Goss, Hanhart, and Ingold, *loc. cit.*). Benzoic acid was not obtained, and an experiment designed to detect the evolution of small amounts of ethylene also yielded a negative result.

(III). *Attempted Preparation of* p-*Nitrodi*(β-*phenylethyl*)*dimethylammonium Chloride from* β-*Phenylethyl Chloride and* p-*Nitro*-β-*phenylethyldimethylamine; Formation of* p-*Nitrostyrene,* β-*Phenylethyldimethylamine and Di*(β-*phenylethyl*)*dimethylammonium Chloride.*—We regard these experiments as showing that the *p*-nitrodi-(β-phenylethyl)dimethylammonium ion is unstable under the experimental conditions owing to the great tendency to the elimination of the *p*-nitrophenylethyl group as nitrostyrene. The only quaternary salt which could be isolated from the product of interaction of β-phenylethyl chloride and *p*-nitro-β-phenylethyldimethylamine was di(β-phenylethyl)dimethylammonium chloride, the formation of which we explain as follows:

$$\left.\begin{matrix} NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2 \\ C_6H_5\cdot CH_2\cdot CH_2Cl \end{matrix}\right\} \rightarrow \left[\begin{matrix} NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2 \\ C_6H_5\cdot CH_2\cdot CH_2 \end{matrix}\!\!\times\!\!\overset{+}{N}Me_2\right] \rightarrow \left\{\begin{matrix} NO_2\cdot C_6H_4\cdot CH{:}CH_2 \\ C_6H_5\cdot CH_2\cdot CH_2\cdot NMe_2 \end{matrix}\right.$$

$$[(C_6H_5\cdot CH_2\cdot CH_2)_2NMe_2]'Cl'$$

Experiments were carried out under various conditions, but with substantially identical results; the following is typical.

p-Nitro-β-phenylethyldimethylamine, liberated from 20 g. of the pure oxalate, was heated with a slight excess of β-phenylethyl chloride for 48 hours on the water-bath, and the partly solid reaction product was shaken with water and ether. The ethereal layer contained no bases, but only an olefinic substance together with the excess of β-phenylethyl chloride. The residue obtained on evaporation was treated with bromine, and the solid dibromide identified as *p*-nitrostyrene dibromide by direct comparison with a genuine specimen and by oxidation by means of permanganate to *p*-nitrobenzoic acid. No styrene dibromide could be found.

The aqueous solution was basified and extracted with ether, and the ethereal solution precipitated by picric acid dissolved in benzene. The picrates (10 g.) consisted of a mixture of β-phenylethyldimethylammonium picrate (about one-third) and *p*-nitro-β-phenylethyldimethylammonium picrate (about two-thirds), which were readily separated by crystallisation from alcohol containing 10% of acetone, the former salt remaining in the solution.

The alkaline aqueous solution was filtered, neutralised, and precipitated with aqueous sodium picrate; the crude *di*(β-*phenylethyl*)*dimethylammonium picrate* thus obtained crystallised from alcohol in orange-yellow plates (8 g.), m. p. 111—112° (Found: C, 60·5; H, 5·4; N, 11·8. $C_{24}H_{26}O_7N_4$ requires C, 59·8; H, 5·4; N, 11·6%). This compound was also prepared by heating 33% alcoholic dimethylamine solution with excess of β-phenylethyl chloride in a sealed tube at 90° for 16 hours. The *hydrochloride* was thus obtained in good yield. It is readily soluble in water, alcohol, acetone, and chloroform, and separates from the last or from acetone–benzene in colourless needles, m. p. 70°. It is insoluble in ether and benzene and is not hygroscopic. On treatment with sodium picrate solution the above picrate is formed.

Decomposition of di(β-*phenylethyl*)*dimethylammonium hydroxide.* An aqueous solution of the hydroxide rapidly decomposed when boiled, the products being styrene, which was identified as its bromide, and β-phenylethyldimethylamine, identified as picrate.

β-*p*-Nitrophenylethyldimethylamine was prepared by heating β-*p*-nitrophenylethylamine hydrochloride (9 g.) with 20 c.c. of 40% formaldehyde under pressure at 135°. The chloride thus obtained was converted into the oxalate, which was twice crystallised from 95% alcohol (yield of pure oxalate, 10·5 g.). The more rapid but less economical method of heating the primary hydrochloride (2 parts) with paraformaldehyde (1 part) for 1 hour in an open

flask at 150° was also employed; complex condensation products were formed which impaired the yield.

(IV). *β-Aminodimethyldiethylammonium Hydroxide, β-Dimethylaminodimethyldiethylammonium Hydroxide, s-Tetramethyldiethylethylenediammonium Dihydroxide, Hexamethylethylenediammonium Dihydroxide, and their Intermediates.*—The first of these bases, $(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2Et)^{\cdot}OH'$, was prepared by hydrolysis of the condensation product, $\{C_6H_4{\cdot}(CO)_2{\cdot}N{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2Et\}^{\cdot}Br'$, of phthal-β-bromoethylimide and dimethylethylamine.

Phthal-β-bromoethylimide (10 g.), absolute alcohol (15 c.c.), and 25% alcoholic dimethylethylamine (11 g. of solution) were warmed together in a sealed tube with frequent shaking until a homogeneous liquid resulted. The tube was then heated for 6 hours at 120°, and opened while still warm, since, on cooling, a very stiff cake of crystals is obtained. After being washed with absolute alcohol, the *β-phthalimidodimethyldiethylammonium bromide* was almost pure, m. p. 280° (decomp.); the yield (about 60%) could be slightly increased by working up the alcoholic filtrate. The salt is extremely soluble in water and is conveniently crystallised by dissolving it in a little water, warming, and adding much absolute alcohol; it then separates in pearly leaflets (Found: C, 51·4; H, 6·2. $C_{14}H_{19}O_2N_2Br$ requires C, 51·4; H, 5·8%).

The bromide was boiled with 20% hydrochloric acid (6 parts) for 6 hours and the cooled solution was filtered from phthalic acid and evaporated to dryness. A solution of the residue in a little water was filtered from a small quantity of phthalic acid and treated with sodium picrate solution. *Dimethylethylethylenediammonium dipicrate*, $\{NH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2Et\}^{\cdot\cdot}\{O{\cdot}C_6H_2(NO_2)_3\}'_2$, separates from hot water in well-formed, lemon-yellow leaflets, m. p. 198° (decomp.) (Found: C, 37·3; H, 4·1. $C_{18}H_{22}O_{14}N_8$ requires C, 37·6; H, 3·8%).

Tetramethylethylenediamine has been prepared by Freund and Michaels (*Ber.*, 1897, **30**, 1385) from ethylene dibromide and dimethylamine. The bromide (14 g.) and the base (20 g. of a 33% alcoholic solution) were heated for 3 hours at 100° under pressure, and the salt was washed with alcohol and distilled with potassium hydroxide. The base was dried by distillations over potassium hydroxide and barium oxide (yield 5·6 g.).

Attempts to prepare the same compound by methylating ethylenediamine with paraformaldehyde were unsuccessful when free ethylenediamine or its hydrochloride was used, but succeeded with the sulphate. The yield is only 40%, but the method is rapid and convenient. A solution of ethylenediamine (40 g.) in absolute alcohol was neutralised with concentrated sulphuric acid and the

precipitated salt was collected and dried. An intimate mixture of this with paraformaldehyde (90 g.) was heated under reflux, melting and frothing commencing at 90°. The internal temperature was maintained between 130° and 140° for 4 hours. After cooling, the product was mixed with concentrated aqueous potassium hydroxide and distilled (b. p. about 95°), and the distillate was dried with solid potassium hydroxide and distilled over barium oxide; the main portion boiled at 121—122·5°. The dipicrate is sparingly soluble, but separates from aqueous acetone in yellow needles, m. p. 263° (decomp., becoming brown at 250°) (Knorr, *Ber.*, 1904, **37**, 3509, gives 252° as the m. p. of an unrecrystallised specimen).

An ethereal solution of tetramethylethylenediamine was allowed to react with ethyl iodide (1 mol.) for several days. Small white needles, a liquid, and large needles were successively deposited. The precipitate was washed with ether by decantation, exposed in a desiccator until completely solid, and then crystallised from hot alcohol. *s-Tetramethyldiethylethylenediammonium di-iodide* separated in large, colourless needles, which lost their lustre in a desiccator or in air; m. p. 233° (decomp.) (Found: C, 28·1; H, 6·4. $C_{10}H_{26}N_2I_2$ requires C, 28·0; H, 6·1%). The salt is readily soluble in water and gives a neutral reaction. On addition of aqueous sodium picrate, the *dipicrate* is precipitated, which separates from aqueous acetone–alcohol in small, flattened needles, m. p. 261° (decomp.) (Found: C, 42·2; H, 4·9. $C_{22}H_{30}O_{14}N_8$ requires C, 41·9; H, 4·7%).

The alcoholic filtrate obtained in the preparation of the di-iodide was evaporated in a vacuum to a thick syrup, which had a strongly alkaline reaction and was soluble in chloroform. Its solution in alcohol was mixed with alcoholic hydrogen chloride and the pale brown hygroscopic salt was collected and converted into the picrate, which, after crystallisation from aqueous acetone–alcohol, had m. p. 212—214°. The same picrate was obtained when tetramethylethylenediamine was allowed to react with a small quantity of ethyl iodide without a solvent for 48 hours at the ordinary temperature. The solid iodide, which was collected and washed with ether, was hygroscopic and its aqueous solution had an alkaline reaction. The addition of aqueous sodium picrate yielded a precipitate having m. p. 210—214°. A similar but less pure product, m. p. 207—214°, was obtained in small amount, along with a large quantity of the diammonium iodide, m. p. 233°, when excess of ethyl iodide was employed. The m. p. (212—214°) of *β-dimethylaminodimethyldiethylammonium picrate* is depressed to about 205° by admixture with the dipicrate (m. p. 261°), but analysis indicates the presence of a small amount of this salt which we were

unable to remove (Found: C, 44·6; H, 5·8. $C_{14}H_{23}O_7N_5$ requires C, 45·0; H, 6·2%).

Hexamethylethylenediammonium dipicrate, orange-yellow needles, m. p. 285° (decomp.), was prepared by mixing tetramethylethylenediamine with trinitroanisole (2 mols.) in benzene solution. It was crystallised from a large volume of hot water (Found: C, 40·1; H, 4·4. $C_{20}H_{26}O_{14}N_8$ requires C, 39·9; H, 4·3%).

Decomposition of β-aminodimethyldiethylammonium hydroxide. The aqueous solution obtained by shaking a suspension of the picrate in hydrochloric acid with benzene was concentrated to a syrup, diluted, and decomposed with water and excess of silver oxide; the filtered solution was then distilled in the usual apparatus. A portion of the solution in the 3*N*-hydrochloric acid trap was distilled and the first fraction of distillate, which strongly reduced Fehling's solution, was treated with *p*-nitrophenylhydrazine, acetaldehyde-*p*-nitrophenylhydrazone being obtained.

The solution in the bromine trap was mixed with ice, decolorised with sulphur dioxide, rendered alkaline, and extracted with light petroleum; ethylene dibromide, b. p. 131°, was then obtained in 45% yield (Found: C, 12·9; H, 2·3; Br, 84·9. Calc.: C, 12·8; H, 2·1; Br, 85·1%).

The acid solutions were evaporated to dryness and the hygroscopic residue was mixed with solid potassium hydroxide and distilled at 60°. The distillate was collected in ether and treated with picric acid in benzene, and the precipitate was crystallised twice from alcohol, pure dimethylethylammonium picrate being obtained (yield 19%). The residual bases were then completely distilled and boiled with alcoholic methyl sulphate and anhydrous sodium carbonate for 2 hours. On adding water, boiling off the alcohol, and adding sodium picrate solution in excess, a precipitate was obtained which, after two crystallisations from boiling water, yielded pure hexamethylethylenediammonium dipicrate, identical with the specimen described above (yield 30%).

Decomposition of β-dimethylaminodimethyldiethylammonium hydroxide. The solution of the hydroxide was prepared and distilled as in the last example, and the ethylene dibromide (yield 48%) isolated in the same way. The bases were also worked up in a similar manner, excepting that the tetramethylethylenediamine was purified through its sparingly soluble picrate and was not converted into the quaternary compound. The yield of dimethylethylammonium picrate was 20% and of the diammonium dipicrate 28%.

(V). *β-Hydroxydimethyldiethylammonium Hydroxide.*—β-Hydroxydimethylethylamine was prepared by a modification of Knorr and

Matthes's method (*Ber.*, 1901, **34**, 3482). Ethylene oxide (20 g.) was added to 64 g. of 33% aqueous dimethylamine previously diluted with ice-water. The product was distilled, the first 20 c.c. being rejected, up to 136°, and the distillate was saturated with potassium hydroxide and extracted with ether. The extract was dried with sodium sulphate and with solid potassium hydroxide, and the ether distilled up to 40°. Barium oxide was then added, and the aminohydrin distilled, b. p. 130—133°.

The reaction with ethyl iodide takes place on warming in ethereal solution, the product separating in colourless needles, which may be accompanied by a viscous liquid if the hydroxy-base used is not perfectly dry. In the latter case the liquid product may be caused to solidify by desiccation. β-*Hydroxydimethyldiethylammonium iodide* is excessively soluble in water and alcohol and is very hygroscopic. The *picrate* separates from water or alcohol in long needles, m. p. 237—239°. It is easily soluble in hot water and alcohol and very easily soluble in acetone (Found : C, 42·0; H, 5·2; N, 16·4. $C_{12}H_{18}O_8N_4$ requires C, 41·6; H, 5·2; N, 16·2%). It forms two modifications, the more stable having m. p. 258°.

Distillation of the hydroxide. The quaternary hydroxide prepared from the iodide and silver oxide was distilled as usual. Much frothing occurred. Acetaldehyde was identified through its *p*-nitrophenylhydrazone, as in Section IV, and ethylene as its dibromide (yield 37%). The acid solution was evaporated and the residue was covered with ether and basified with solid potassium hydroxide. The ethereal extract was dried with sodium sulphate and distilled over barium oxide. The main portion of the ethereal distillate, on treatment with a benzene solution of picric acid, yielded pure dimethylethylammonium picrate. The last portion, which was collected separately, on similar treatment gave a mixture of picrates (m. p. 190—195°) from which the same pure picrate (m. p. 202—203°) was obtained by crystallisation from alcohol (total yield, 26%). The β-hydroxydimethylethylamine passed over at about 100—135° and was purified through its picrate (Knorr and Matthes, *loc. cit.*).

(VI). β-*Chlorodimethyldiethylammonium Hydroxide.*—β-Chlorodimethylethylamine was prepared by Knorr (*loc. cit.*) by heating β-hydroxydimethylethylamine with fuming hydrochloric acid at 180°. The following process is less laborious.

A chloroform solution of β-hydroxydimethylethylamine, obtained from 30 g. of ethylene oxide as described in Section V, was well cooled and slowly treated with thionyl chloride until the two liquid layers at first produced became one. The solution was then heated under reflux, and the crystals, which commenced to separate after

15 minutes, were collected after the mixture had boiled for 2 hours and cooled. They were washed with a little chloroform and dried in a desiccator. In this way, 33 g. of almost pure β-chlorodimethylethylammonium chloride were obtained in colourless, hygroscopic needles, m. p. 200°. The thionyl chloride filtrate was distilled, and the brown mass of crystals was washed with ether and crystallised from a little absolute alcohol (yield, 6 g.; m. p. 196°). The corresponding *picrate* separated from 95% alcohol in large leaflets, m. p. 126—127° (Found: C, 36·1; H, 4·3. $C_{10}H_{13}O_7N_4Cl$ requires C, 35·7; H, 3·9%).

An aqueous solution of the above chloride (30 g.) was mixed with concentrated potassium hydroxide, and the base extracted with ether. Most of the ether was evaporated and the concentrated ethereal solution was warmed for several hours with excess of ethyl iodide. The crystalline product was extracted with hot alcohol, which left undissolved a small amount of tetramethylpiperazinium dichloride (m. p. 304°, decomp.), and the *β-chlorodimethyldiethylammonium iodide*, which separated, on cooling, in needles, m. p. 198° (Found: C, 27·2; H, 5·7. $C_6H_{15}NClI$ requires C, 27·3; H, 5·7%), was converted into the *picrate* by precipitation from aqueous solution with sodium picrate. This salt forms long, transparent, yellow needles, m. p. 192—193° (Found: C, 39·2; H, 4·8. $C_{12}H_{17}O_7N_4Cl$ requires C, 39·5; H, 4·7%).

Decomposition of β-chlorodimethyldiethylammonium hydroxide. The hydroxide appeared to be stable in boiling aqueous solution, but as soon as the water was driven off a violent reaction set in. The main basic product was dimethylethylamine, which was isolated as picrate in the usual way. Only traces of gaseous olefin were collected in the bromine, and in the distilling flask an amorphous product remained which contained chlorine and nitrogen but was insoluble in the usual solvents.

(VII). *Trimethyl-n-propylammonium Hydroxide.*—Collie and Schryver showed that the main products of decomposition were trimethylamine and propylene; analytical data indicated that dimethylpropylamine also was produced in small amount. The solution obtained by treating trimethyl-*n*-propylammonium iodide with silver oxide and water was concentrated by distillation (the distillate did not contain more than a trace of trimethylamine) and then distilled through the usual series of traps. The yields of methyl alcohol, isolated as methyl *p*-nitrobenzoate, ranged from 4 to 7%. Experiments with artificially prepared, dilute solutions of methyl alcohol showed that this method of isolation is by no means quantitative, and hence the amount of methyl alcohol formed must have been considerably greater than that stated

above. Nearly pure propylene dibromide, b. p. 134—141°, the main part having b. p. 139—140° (Found: C, 18·1; H, 2·9; Br, 79·2. Calc.: C, 17·8; H, 3·0; Br, 79·2%), was obtained in 81% yield. Preliminary experiments showed that the absorption of the olefin was quantitative and took place entirely in the first bromine trap. After successive treatment with ice, sulphur dioxide and sodium hydroxide (slight excess), the bulk of the bromide was run off, and the remaining trace extracted with a little petroleum (b. p. 40—45°). The mixture of bromide and petroleum was dried with calcium chloride and distilled through a cooled column. The yield recorded above includes a correction (2·6%) for the weight of vapour filling the flask at the boiling point up to the level of the side arm. Our practice in this and similar experiments was to calculate this correction from the gas laws and also weigh the drop of liquid which condensed in the flask on cooling; usually both estimates agreed, but in the event of disagreement, the smaller value was regarded as the correction. A small correction is also applied for the volatility of the bromide in the ligroin vapour. The yield of mixed quaternary picrates obtained from the mixed bases and trinitroanisole was 89% (m. p. about 190°) and a single crystallisation from 95% alcohol yielded 78% (*i.e.*, 87·5% of the mixture) of pure tetramethylammonium picrate (Found: C, 40·4, 40·2; H, 4·7, 4·9; N, 18·5. Calc. for tetramethylammonium picrate: C, 39·7; H, 4·6; N, 18·5. Calc. for trimethylpropylammonium picrate: C, 43·7; H, 5·5; N, 17·0%). From the carbon content, the mixture contains 15% of trimethylpropylammonium picrate, *i.e.*, 14 molecules %, which agrees with the yield of propylene dibromide to within the limits of analytical accuracy. A small quantity of trimethylpropylammonium picrate was isolated from the residues of the crystallisation, as follows: the alcoholic mother-liquors were evaporated and the residue was boiled for a short time with benzene containing 5—10% of acetone, in which mixture the tetramethylammonium salt is scarcely soluble. The filtered solution yielded leaflets on cooling, which, after two crystallisations from water and two from methyl alcohol, gave stout, yellow crystals, m. p. 195—196°, consisting of pure *trimethyl*-n-*propylammonium picrate* (Found: C, 43·5; H, 5·6; N, 16·7%). This salt is much paler in colour than the tetramethylammonium salt and the progress of the separation can to some extent be followed visually. In another experiment, 6% of pure *dimethyl*-n-*propylamine*, b. p. 65—66°, was isolated by distillation of the mixed tertiary bases first over barium oxide and then over sodium (identified as picrate).

(VIII). *Trimethyl*-n-*butylammonium Hydroxide*.—These experi-

ments were carried out in precisely the same way as those described in Section VII. We isolated 12—14% of methyl *p*-nitrobenzoate and, taking precautions to avoid loss (above), 75% (corr.) of almost pure αβ-dibromobutane, b. p. 160—165°. The carbon content of the mixed picrates (yield 93%) obtained by treating the basic product with trinitroanisole indicated the presence of 23% of trimethyl-*n*-butylammonium picrate, *i.e.*, 21 molecules %, in fair agreement with the estimate based on the yield of dibromobutane.

These results differ considerably from those of von Braun (*loc. cit.*), who claims to have obtained 50% of dried and fully rectified dimethyl-*n*-butylamine, b. p. 96°. Working on the same scale (31 g. of trimethyl-*n*-butylammonium iodide) and dehydrating the mixed bases with potash and with metallic sodium as he recommends, we obtained only 1·65 g., *i.e.*, 13%, of almost pure butyl base, b. p. 93—96°. It is difficult to avoid losses in the isolation of this substance when working on so small a scale, but it is evident from the data recorded above that von Braun's yield is much too high.

(IX). *Trimethyl*-sec.-*butylammonium Hydroxide.*—*sec.*-Butylamine was methylated with excess of methyl iodide in moist ether to which successive quantities of silver oxide were added. After addition of water and filtration, the aqueous layer was extracted with ether, titrated, and distilled. The yield of αβ-dibromobutane was about 65%, and the basic fraction consisted very largely of trimethylamine and did not contain an isolable quantity of dimethyl-*sec.*-butylamine. A portion of the liquid obtained on distilling the dilute hydrochloric acid solution in which the basic decomposition products had been collected was turbid and had the odour of *sec.*-butyl alcohol, and the methyl *p*-nitrobenzoate, obtained in very small amount from the early fractions of the distillate, was sticky, probably owing to the presence of the butyl ester. On account of the limited quantity we were able only to drain the crude methyl ester and crystallise it once, but the m. p. (88—91°) of the specimen so obtained was raised by admixture with pure methyl *p*-nitrobenzoate.

(X). *Trimethyliso**butylammonium Hydroxide.*—These experiments were carried out like those described in Sections VII and VIII, but a slight complication arose owing to the fact that, when the evolved *iso*butylene was passed into ice-cooled bromine, not only addition, but also a little substitution occurred with the production of hydrogen bromide. Therefore, on distilling the bromide, in addition to a considerable quantity (usually about 50%) of almost pure αβ-dibromo*iso*butane, b. p. 147—153° (Found: C, 22·4; H, 3·9. Calc.: C, 22·2; H, 3·7%), a less volatile portion was

obtained having a higher proportion of bromine and lower proportions of carbon and hydrogen than correspond with the formula $C_4H_8Br_2$. This was weighed (x grams) and analysed (C, p%), and the corresponding weight of *iso*butylene taken as 0·0117 px. The mean of three concordant estimates of the total quantity of *iso*butylene produced was 63%. Methyl alcohol was qualitatively identified in the usual way (17% of methyl *p*-nitrobenzoate isolated). The basic fraction consisted mainly of trimethylamine, but also contained *dimethylisobutylamine* (Found : C, 71·1; H, 15·0. $C_6H_{15}N$ requires C, 71·3; H, 14·85%), 20—25% of which was isolable in a pure condition (b. p. 80—81°; distilled over sodium). *Dimethylisobutylammonium picrate* separates from methyl alcohol in canary-yellow prisms, m. p. 124° (Found : C, 43·7; H, 5·7. $C_{12}H_{18}O_7N_4$ requires C, 43·7; H, 5·5%), and *trimethylisobutylammonium picrate*, prepared from the tertiary base and trinitroanisole, crystallises from water in orange-yellow needles, m. p. 173—174° (Found : C, 45·5; H, 5·9. $C_{13}H_{20}O_7N_4$ requires C, 45·4; H, 5·8%).

These results differ from those recorded by Collie and Schryver (*loc. cit.*), who obtained only traces of olefin, whilst dimethyl*iso*butylamine was their sole basic product.

(XI). *Trimethyl*-tert.-*butylammonium Hydroxide*.—These experiments were carried out like those in Section IX, with comparable results, excepting that some substitution occurred in the bromine solution. Traces of methyl alcohol were detected, but the precipitated nitrobenzoic ester was oily and could not be fully purified. From the fact that on distilling the dilute hydrochloric acid solution there was an arrest at 80° we infer the probable presence of *tert.*-butyl alcohol. Methylation of the basic fraction with trinitroanisole showed that trimethylamine was the principal constituent.

(XII). *Trimethyl*-sec.-*amylammonium Hydroxide*.—The procedure and results were similar to those of the preceding section. Traces of impure methyl *p*-nitrobenzoate, m. p. 85—90°, were obtained, together with αβ-dibromopentane, b. p. 185—190°, and trimethylamine. The formation of *n-sec.*-amyl alcohol was observed (compare Section IX), but it was not isolated. The tertiary base was identified by conversion into tetramethylammonium picrate.

(XIII). *Trimethyl*-β-*ethyl*-n-*butylammonium Hydroxide*.—β-Ethyl-*n*-butylamine (ψ-hexylamine) was prepared as recommended by Freund and Hermann (*Ber.*, 1890, **23**, 192), and the fraction, b. p. 120—123° (Found : C, 71·0; H, 15·0. Calc. : C, 71·3; H, 14·85%), methylated as described in Section IX. A considerable yield (30%) of methyl *p*-nitrobenzoate was obtained. Substitution occurred in the bromine solution, as was shown by the production of hydrogen bromide, and therefore, since the quantity of material

was rather limited, the mixed bromides were not distilled, but were analysed (Found: C, 28·3; H, 4·6%), and the weight of olefin was calculated from the carbon content by the formula 0·0117 px, giving the value 43% of the theoretical. This figure was confirmed by analysis of the mixed picrates (yield 94%) obtained by treating the basic fraction with trinitroanisole (Found: C, 45·0; H, 5·8. Calc. for tetramethylammonium picrate: C, 39·7; H, 4·6. Calc. for trimethylhexylammonium picrate: C, 48·4; H, 6·4%. Hence, proportion of tetramethylammonium picrate = 39%, *i.e.*, 43 molecules %).

(XIV). *Trimethyl*-β-n-*propyl*-n-*amylammonium Hydroxide*.—The primary base, prepared as in the preceding case *via* di-*n*-propylacetonitrile, had b. p. 163—165° (Errera, *Gazzetta*, 1896, **26**, ii, 246, gives b. p. 167° corr.). The yield of methyl *p*-nitrobenzoate was 39%. The yield of olefin determined as in the preceding experiment was 31%, and analysis of the mixed quaternary picrates indicated the presence of 29 molecules % of tetramethylammonium picrate.

(XV). *Trimethyl*-n-*propylammonium Phenoxide*.—The quaternary iodide was converted into the hydroxide, the solution of which was concentrated until it *began* to decompose. (This point is readily ascertained from the fact that the steam entering the first acid trap is not quite completely condensed, minute residual bubbles reaching the surface.) Phenol was then added (1·05 equivs.). The incipient decomposition then ceased and a further quantity of water had to be driven off, and the temperature raised, before it recommenced, indicating the greater stability of the phenoxide than the hydroxide. The solution was distilled to dryness, the anisole collecting as an oil in the first hydrochloric acid trap. It was extracted with light petroleum, washed with sodium hydroxide and distilled (yield, 65%), b. p. 153—156° (Found: C, 77·7; H, 7·5. Calc.: C, 77·8; H, 7·4%). The bases were converted into the quaternary picrates with trinitroanisole (yield 93%), and analysis of the mixture indicated that trimethyl-*n*-propylammonium picrate and tetramethylammonium picrate were present in the proportion 3 : 1. Both picrates were isolated by crystallisation as described above. The yield of nearly pure propylene dibromide, b. p. 135—141°, was 15%.

(XVI). *Trimethyl*-n-*propylammonium Carbonate*.—The hydroxide solution was saturated with pure carbon dioxide and distilled as usual. Methyl alcohol was formed in considerable quantity and isolated as the *p*-nitrobenzoate. The yield of propylene dibromide was 26% (uncorr.). A portion of the hydrochloric acid solution was basified in presence of ether, and the picrates (m. p. 110—115°)

precipitated with ethereal picric acid. They were dissolved in hot benzene, and, a certain time having been allowed for crystallisation, the still warm solution was diluted to twice its volume and at once filtered. The residue, after three crystallisations from alcohol, yielded pure trimethylammonium picrate, m. p. 215—216°. On evaporating the benzene solution and crystallising the residue repeatedly from ethyl acetate, pure dimethyl-*n*-propylammonium picrate, m. p. 108—109°, was obtained. Another portion of the acid solution was basified under ether, and the bases were methylated with trinitroanisole (yield 92%). Tetramethylammonium picrate, m. p. 306°, was obtained by crystallisation from alcohol, and trimethyl-*n*-propylammonium picrate, m. p. 194—195°, was isolated from the mother-liquors as previously described. Analyses of the mixed tertiary and quaternary salts indicated the proportion 3 : 1, the propyl derivatives preponderating.

(XVII). *Trimethyl*-n-*propylammonium* m-*Nitrophenoxide*.—This experiment was carried out in the same way as the preceding one, except that *m*-nitrophenol was added in place of phenol. *m*-Nitroanisole, m. p. 37—38°, was obtained in 89% yield by extracting the hydrochloric acid solution with ether, washing the extract with alkali, and evaporating it. A little olefin bromide was produced, but it was not enough to distil, and the base consisted almost wholly of *dimethyl*-n-*propylamine*, 84% of which was obtained in a pure condition (b. p. 65—66°; distilled over sodium) (Found : C, 68·8; H, 15·0. $C_5H_{13}N$ requires C, 69·0; H, 14·9%).

(XVIII). *Trimethyl*-n-*propylammonium Acetate*.—The hydroxide solution was exactly neutralised with acetic acid and distilled. Very little gas passed into the bromine, and, on removing the excess of halogen, only a few drops of oil, insufficient for distillation, remained. Methyl acetate was obtained in quantity by distilling the hydrochloric acid solution and redistilling the first portion of the distillate over calcium chloride; it was identified by its odour, boiling point, and by saponification, the methyl alcohol being characterised by means of its *p*-nitrobenzoate. The picrate obtained from the basic product had m. p. 104—106°, and 2·50 g., on crystallising from ethyl acetate, gave 2·25 g. of pure dimethylpropylammonium picrate, m. p. 107—108·5°. The quaternary picrates obtained by methylating the bases with trinitroanisole had m. p. 204—206°. Several crystallisations from water lowered this m. p. to 195—196°, the m. p. of pure trimethyl-*n*-propylammonium picrate. Since admixture with tetramethylammonium picrate raises the m. p. of trimethyl-*n*-propylammonium picrate, this is the behaviour to be expected if the original mixture contained a small proportion of tetramethylammonium picrate; the colour of the mixed salts also

suggested the presence of a small amount of this substance, but we were not able to isolate it. Artificial mixtures of trimethyl-*n*-propylammonium picrate and tetramethylammonium picrate containing 9—10% of the latter behaved in all respects similarly, and we have little doubt that a small proportion of tetramethylammonium picrate was contained in the product obtained from the bases formed by decomposition of trimethyl-*n*-propylammonium acetate.

(XIX). *Trimethyl*-n-*propylammonium chloride* was prepared and distilled in the same way as the acetate. The yield of propylene dibromide, b. p. 139—140°, was 10% (uncorr.). The quaternary picrates obtained from the basic decomposition products and trinitroanisole had m. p. 213—222°, and on crystallisation from 95% alcohol yielded, first, pure tetramethylammonium picrate and then a mixture. When the latter *began* to be deposited, the solution was diluted with warm alcohol and filtered. The residue obtained on evaporating the filtrate, on repeated crystallisation from water, yielded trimethyl-*n*-propylammonium picrate, m. p. 195—196°. The non-volatile residue remaining in the flask consisted of a mixture of the chlorides of trimethylamine and dimethyl-*n*-propylamine, and on methylating the liberated bases, the corresponding quaternary picrates were obtained.

(XX). *Trimethyl*-n-*propylammonium Iodide*.—The results were comparable in all respects with those recorded in the preceding paragraph, except that the yield of propylene dibromide (13%) was a little greater.

We wish to thank the Royal Society for defraying part of the cost of this investigation.

THE UNIVERSITY, LEEDS. [*Received, February 19th*, 1927.]

CXL.—*The Passivity of Metals. Part I. The Isolation of the Protective Film.*

By ULICK RICHARDSON EVANS.

THE alteration in chemical properties conferred on iron and other metals by oxidising treatment has been attributed by some investigators to a protective film of oxide, oxygen-alloy, or other material, and by others to some essential change in the metal itself, or to the removal of a supposed catalyst. Many chemists have hesitated to accept the oxide-film theory chiefly because (1) no film is usually visible, and (2) iron which has been covered with a visible film by heating is often not passive. However, recent

work (Evans, *Nature*, 1926, **118**, 51) has shown that electrolytic iron exposed to air or oxygen at different temperatures undergoes absolutely no *visible* change until the oxide film reaches the thickness requisite to give the first yellow interference tint. Thinner films are quite invisible, and yet they give good protection against attack by copper nitrate—better protection, in fact, than thick visible films, which fail locally at points representing pores or cracks, causing deposition of copper on the outer surface of the oxide scale. It is noteworthy that pure iron, rendered active by abrasion, becomes passive when exposed for a few hours to dry air at the ordinary temperature.

It seems at least possible that the production of passivity upon iron by immersion in solutions of oxidising agents, or by anodic treatment in an alkaline liquid, may be due to films too thin to give interference colours. Indeed, it is clear that the greater the specific protective character of the material composing the film the less likely is the thickness to reach the visible range, since the film will hinder its own growth by excluding the oxidising agent from the metal below; only when the protective character of the material is imperfect is a visible film to be expected. This is found to be the case. Ordinary anodic treatment in sodium hydroxide solution renders iron passive, but produces no visible change; if an alternating current is superimposed on the direct current, however, attack upon the iron occurs, and colours (straw-yellow, gold, reddish-brown, and purple) appear in turn on the iron (Allmand and Barklie, *Trans. Faraday Soc.*, 1926, **22**, 34). Likewise, immersion of iron in pure potassium chromate solution causes no corrosion and produces no marked change in appearance; but if a chloride is present in the chromate solution, corrosion occurs locally, and around the points of attack bright colours (yellow, red-mauve, and blue) may be seen, similar to those obtained by heating iron in air at high temperatures (Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163T). Again, specimens of zinc partly immersed in sodium chloride solution develop colours over a zone near the water line; after drying in air, this zone is found to be blackened by copper sulphate solution more quickly than the parts of the zinc displaying no visible film (Evans, *Ind. Eng. Chem.*, 1925, **17**, 366).

In such cases, the very fact that the film has become thick enough to give colours is a sign that it is imperfectly protective. An efficient protective film will nearly always be invisible as long as it is in optical contact with highly reflecting metal. It is true that sometimes a considerable deposit can be seen on metal which has been rendered passive, but the incoherent appearance of such

deposits is sufficient to show that they are not protective films, although their presence is evidence that the liquid is saturated with some compound—a condition favourable for the production of a true film. The arrival and departure of such deposits do not always correspond to the arrival and departure of passivity (compare Müller, *Z. Elektrochem.*, 1924, **30**, 401; Hedges, J., 1926, 2878).

The rational method of rendering visible a film too thin to give interference tints is to separate it from the metallic basis by dissolving away the latter from underneath; films of such thicknesses are readily visible if backed by air or a medium such as water, which has no great reflectivity. Various early attempts by the author to isolate in this way a film from passive iron were unsuccessful, probably owing to the presence of a second phase (*e.g.*, cementite, Fe_3C) which could not easily be dissolved away with the metal. Through the kindness of Dr. W. H. Hatfield, who has provided a considerable quantity of electrolytic iron, this obstacle now has been removed. The material had been fused in a vacuum in a magnesia crucible before being rolled into sheets 0·12 mm. thick. Analysis showed C, 0·04; Mn, 0·025; Si, 0·010; S, 0·013; P, 0·017; Ni, 0·09%. The main impurity (nickel) would certainly be present in solid solution, and could therefore be considered harmless. Photomicrographs of the material showed a satisfactory absence of inclusions.

Before each experiment, except where otherwise stated, the iron was ground with washed emery flour, applied on unbleached linen, which had previously been boiled out with water; it was then rubbed with filter paper. In special cases, emery paper, in seven grades of coarseness, was employed, whilst in one series of experiments a carborundum disc was used to abrade the surface.

Anodic Method of removing Transparent Skin from Passive Iron.—Specimens of iron rendered passive by immersion in a solution of potassium chromate, potassium nitrite, or sodium hydroxide, or by exposure to dry air, were subjected to anodic treatment, so as to dissolve away the metallic iron from the interior and leave the skin. This result could be obtained under a fairly wide range of conditions. In a typical experiment, a strip of iron 0·5 cm. wide was immersed in $M/20$-potassium chromate solution for $2\frac{1}{2}$ hours at 22°, and was then washed and dried; the bottom of the strip was trimmed off, and the specimen was then clamped vertically in $N/10$-sodium chloride solution, so that only the lowest 1 cm. was actually immersed, and subjected to anodic treatment with a current of 6 milliamps.; precautions were taken that the cathodically-produced alkali did not come near the anode. Dissolution of

the metal started at the bottom, and worked upwards; the action did not cease at the water level, for after about 16 hours the metal just above the water line was quite transparent, the whole specimen retaining essentially its original shape; however, when the transparent zone had spread upwards a few mm. above the water level, the lower portion usually broke off just above the water level, thus stopping the flow of current. Similar results were obtained with iron rendered passive by the other methods mentioned above.

After each experiment, an examination under a binocular microscope was carried out. The envelope of the electrode after anodic treatment consisted of two thin transparent parallel membranes united at the two edges. Between them was enclosed an appreciable quantity of liquid rich in ferrous chloride; a little residual metallic iron was found within the envelope in many specimens, but by far the greater part of the metal had in every case been dissolved away. The enveloping membrane consisted of ferric oxide and, probably owing to its thinness, was only pale yellowish-grey by transmitted light when freed from adhering material; but in nearly every case there was attached to it a quantity of "rusty" ferric hydroxide having a distinct yellowish-brown colour. On the immersed portion, this rusty hydroxide was often observed hanging from the outside in loose tufts, but it also occurred in the interior, where it was unequally distributed in patches clinging rather closely to the inner surfaces of the two membranes. Above the water line there was usually a much smaller amount of the yellowish-brown hydroxide, and for that reason most of the specimens became more completely transparent above the water level than below it. There was also more residual iron in the part below the water line, thus causing local opacity.

There seems but little doubt that the transparent envelope represents a skin present upon the metal before the anodic treatment commenced; the two parallel membranes represent the two surfaces of the original electrode. The envelope preserved in detail the original outline of the specimen; in some cases, the microscope revealed in the transparent skin tiny opaque inclusions arrayed along a series of parallel lines at right angles, unmistakably representing the original grinding directions; these lines are discussed later.

The yellowish "rusty" ferric hydroxide can be regarded as a hydrolysis product of ferric chloride or as an oxidation product of ferrous chloride. A reason for the fact that it occurs more frequently below the water level than above it is suggested by the ordinary principles of probability: above the water line, capillary forces will tend to keep the two parallel membranes close together,

and the volume of iron salt solution enclosed between them will be small; below the water line, slight separation of the two skins may occur, and this fact (along with the possible occurrence of soluble iron salts outside the membrane) accounts for the close packing of the "rusty" patches. In only 3 experiments out of 57 was the *immersed* portion of the electrode converted into a transparent pseudomorph free from the rusty type of hydroxide; but in several cases where the central parts of the immersed portion were rendered almost opaque in places with rusty patches, the edges (where the two membranes necessarily approached close together) were seen to be transparent and nearly colourless.

It was remarkable that the transparent envelope was usually strong enough to retain the shape of the original electrode. The bulging referred to above was usually so slight as almost to escape notice; sometimes, however, the two membranes gaped far apart, with considerable distortion of the whole shape. Occasionally there was a tendency to curl up, whilst not infrequently small local rents occurred on one or both skins. Such imperfections were actually rather useful in revealing the fact that without doubt the transparent skeleton consisted of two separate membranes.

Iodine Method of Removing the Skin.—More definite information regarding the function of the skin in protecting iron was obtained by studying the action of iodine on passive iron; a saturated solution in 10% potassium iodide was found convenient. Pieces of iron were rendered passive in potassium chromate, and a deep scratch was made along the middle of each of them. They were then clamped vertically so as to be partly immersed in the iodine solution. After 2 days, the metal had become corroded through completely at numerous points along the line of the scratch, and usually also at points on the water line. Elsewhere there was no serious loss of thickness, except at isolated points mostly situated near the edges. The greater part of the surface, however, was covered with a transparent film which could easily be removed; below the skin, the metal was distinctly corroded, especially close to the scratch. One specimen removed in the early stages had areas over which the skin, although already visible, was still adherent; around the boundaries of these areas, the corrosion below the skin was very slight. This seemed to show that the detachment of the transparent skin was mainly due to the dissolution of the metal below. No evidence was obtained for the conversion of the metal itself to an inert form as suggested by Russell (*Nature*, 1925, **115**, 455; 1926, **117**, 47). The relative immunity of the unscratched places appears undoubtedly to be due to the fact that the skin obstructs the flow of iodine to them; it may be that a slow passage of iodine

can occur through the film itself, but the attack takes place far more rapidly where the film has been removed, loosened, or undermined, or where cracks exist in it.

Pieces of freshly abraded iron clamped vertically in the iodine solution behaved quite differently, being corroded away completely up to the water line within a day; just above the water line, there remained a transparent zone consisting of a double membrane, evidently caused by the iodine solution rising by capillarity and corroding the metal between the two oxide skins produced by the action of the air.

The transparent skin freshly removed from passive iron after iodine treatment consisted of flakes of appreciable size, curling rolls 2 to 3 mm. long being quite common; these always broke up into microscopic fragments when washed. The flake-fragments were washed repeatedly by decantation until soluble iron salts were removed, and then examined under the binocular microscope. More than 100 different preparations of flakes, derived from iron rendered passive under different conditions, were studied, but the following features were characteristic of practically all.

The flakes consisted of non-magnetic ferric oxide, and were quite transparent; they often showed a tendency to curl into rolls. Each flake when viewed by transmitted light was seen to be covered with a series of dark lines, the nature of which depended on the preliminary abrasion of the iron. If the iron had been ground in one direction only, there was a single series of parallel dark lines on the flakes; if it had been ground in two directions, the flakes displayed two sets of dark lines intersecting at a corresponding angle. When the flakes were viewed by reflected light at a suitable angle, the dark lines were found suddenly to become bright lines, and there is no doubt that they represent the crenulations left on the surface of the iron by abrasion. Thus the film actually represents the oxidised surface of the original specimen of metal. In most preparations, series of opaque particles were also visible, arranged in rows parallel to the dark lines; these were partly residual iron and partly included grains of abrasive. The film showed a marked tendency to break up along lines parallel to the grinding directions, so that the film obtained from iron ground in two directions at right angles tended to produce roughly square or rectangular flake-fragments.

Although the flakes just described represent, beyond all doubt, the original oxidised surface of the metal, they usually carried a certain amount of secondary ferric hydroxide (doubtless due to hydrolysis of ferric iodide) which could be removed by washing with N/10-hydrochloric acid. Experiments performed under the micro-

scope with acid containing thiocyanate showed that most of the dissolution of the adherent hydroxide occurred within 2 minutes, but the flakes themselves remained unchanged even after many hours. Special experiments showed that the flakes were rendered only very slightly thinner after being washed with acid for 3 hours, apart from the removal of hydroxide. However, the flakes which, before washing, appeared rusty yellow to the naked eye, became, after acid-washing, almost white when viewed suspended in water; when examined under the microscope, they still had a very pale, slightly yellowish-grey colour by transmitted light. The existence of the striæ on the flakes makes it easy to distinguish them from any fragments of that membranous ferric hydroxide film which sometimes forms on the air–water interface of ferric salt solutions, as the result of hydrolysis. This membranous hydroxide sometimes reaches "interference-colour thickness," and is entirely different in appearance and properties from the striated films; a long study of the latter made it absolutely certain that these could not be the result of hydrolysis. To avoid any possible mistake, most of the flake preparations mentioned above were obtained by using stoppered vessels entirely filled with iodine solution, thus avoiding the formation of membranous hydroxide altogether. Each preparation was divided into two portions, one only being washed with acid; each portion was examined separately.

Some further information regarding the distribution of iron in the flakes was obtained by treating them with 8% hydrochloric acid containing either ferrocyanide or ferricyanide. The former reagent conferred a beautiful blue tint on the flakes, which nevertheless retained their form for some hours; the dark lines representing the emery grooves became a deeper blue than the rest. This "blueing" treatment was found useful for showing up flakes which were so thin as to cause no appreciable absorption of light. Such flakes had been recognised previously only by the fact that they carried the usual series of dark parallel lines or opaque specks which could be clearly seen, although the material of the flake itself was invisible; the application of the "blueing" method, however, rendered visible the flakes as a whole. Ferricyanide was useful in showing up the particles of residual metallic iron, which produced a deep expanding circle of blue before the main part of the flakes showed any colour at all. Thiocyanate treatment also gave interesting information, but owing to the solubility of ferric thiocyanate a special method of application was necessary. A number of flakes, suspended in a water-drop, were placed on a glass slide under the microscope; the water was sucked away with tiny pointed strips of filter-paper, leaving the flake on apparently dry

glass. Actually, of course, the glass was covered with an invisible film of moisture; consequently, on placing drops of acidified thiocyanate on the glass *near*, but not in contact with, the flakes, these assumed a pink colour within a few seconds, owing to diffusion of the salt through the moisture film.

Films Produced by Exposure to Air.—Strips of electrolytic iron freshly abraded with emery-paper were held at one end and heated red-hot at the other, so as to produce a temperature gradient. This left the iron without visible change at the cold end, but in the centre the three orders of interference tints appeared, whilst at the hot end there was a region covered with comparatively thick scale. The strip was then cooled and quickly cut into sections, which were separately treated with iodine to isolate the oxide film from each. The film peeled off in big flakes which were largest where the film was thickest. These were washed with water (portions of each also with acid) and examined microscopically.

The main portion of the oxide skin, both on the " apparently unchanged " and " interference-colour " regions, consisted of transparent, non-magnetic ferric oxide, similar to that obtained from passive iron. Opaque magnetic scale began to appear as a separate layer below the transparent films about the region of second-order colours, and became very thick at the red-hot end. Confining attention to the ferric oxide film, no sharp transition of properties was noticed on passing from the " unchanged " region to the " interference-colour " region. Apart from a gradual increase of thickness and strength of the films as one passed along the strip, the same characteristics were seen throughout. All the films showed striæ representing the original emery grinding, and in the thicker films the corrugated character of the flakes was conspicuous at the edges. Moreover, except for the very thin film at the cold end, there was a well-marked tendency to break along the directions of abrasion; the very thin flakes from the cold end were much more ragged and tended to shrivel, or to cling together in flocks, making observation difficult.

Ferric oxide films are by no means so transparent as the lead oxide films separated from heat-tinted lead (Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 231), and the light-absorption produced by the thicker films was considerable. The flakes from the second- and third-order regions, although translucent, were dark brownish-grey by transmitted light. With the thinner films, the amount of light transmitted increased; the first-order flakes were brownish- or yellowish-grey, the tint being only very slightly modified by interference (the optical principles involved will be discussed elsewhere). With the films obtained from the " unchanged " region, the light-absorp-

tion diminished still further, but the flakes retained a slight yellowish-grey tinge which was still discernible at a thickness of one-quarter of that of the first " straw-yellow " film. By matching the absorption of two different flakes with points on a wedge-form light-filter, the approximate ratio of the thicknesses could be determined. For instance, it was found that when the iron had been abraded with emery paper of " 1½ grade " (Oakey), the maximum protection of the metal against the action of either copper nitrate or iodine solution was afforded with a film of thickness about 80—90% of that of the " straw-yellow tinted " metal.* Films having a smaller or greater thickness gave less protection against both reagents. The zone of fairly great resistance to iodine extended into the yellow region, but fell off rapidly in the mauve-red, whilst the iron showing the first-order blue was eaten away almost completely in a period which caused very little corrosion of the yellow-tinted metal. Such information, however, has no general significance. As will be explained below, by the use of finer grinding materials, good protection is obtained at thicknesses far below those just quoted; indeed it is not impossible that a continuous unimolecular film extending over stress-free iron would give protection (compare Vernon's results on copper, J., 1926, 2273).

The most surprising result is that the thicknesses of different flakes taken from the same area of the specimen show a considerable variation. This becomes particularly marked in the case of the films responsible for the first-order blue and subsequent tints, and a microscopic study of these has suggested the cause. Such films when freshly removed showed numerous holes, and beside these holes, or covering them, were smaller pieces of film usually attached as " flaps " to the main films. Evidently, then, these thick films have a marked tendency to crack, as suggested by earlier work (*Nature*, 1926, **118**, 51); at each crack oxygen would gain access to the exposed metal and produce a second film below. If after the iodine treatment this second film remains adherent to the first, a local thickening will be visible at the site of the crack; if it does

* The *actual* thicknesses of the " heat-tint " films have long been the subject of discussion. If we adopt the value 2·36 for the refractive index of ferric oxide towards blue light (Kundt, *Wied. Ann.*, 1888, **34**, 484), and if we neglect the error due to the difference between the phase-changes connected with the reflexions at the two interfaces (see Evans, *J. Soc. Chem. Ind.*, 1926, **45**, 211), then the thickness of the first straw-yellow film should be about 400 Å. The thickness cannot be expressed directly in terms of layers of molecules, as this will depend on the crystal-orientation; but it may be stated that *X*-ray studies by Davey (*Physical Rev.*, 1923, **21**, 716) have shown that the side of the equilateral triangle formed by the three oxygen atoms of the Fe_2O_3 molecule is 5·035 Å.

not adhere, a separate specimen of the second film will be obtained, which will in general be thinner than the average thickness proper to the tint under consideration. Evidence of similar thickening around sites of cracks was obtained for films too thin to produce interference tints on some specimens abraded with the carborundum disc; the cracks followed the grinding directions. In general, however, the films freshly separated from the " unchanged " region did not show cracks or holes as long as they were suspended in water, although holes developed when they were dried. The very thin flakes, which have a ragged—as opposed to a square—outline, probably represent fragments of a discontinuous film which did not completely cover the surface of the metal. It is easy to understand why the continuous films of intermediate thickness give better protection than films of greater or smaller thickness.

We have now to consider the cause of the cracks in the thicker films, and of the discontinuity in the thinner films. The cracking in the *thick* film is undoubtedly due to the compressional stresses resulting from the fact that iron oxide occupies a larger volume than the iron required to produce it (compare Pilling and Bedworth, *J. Inst. Metals*, **1923, 29**, 529). The " saucer-shaped " form of scale-fragments sometimes thrown off from heated metals, especially copper, is a visible proof of this compression. Mechanical considerations show that this cracking will occur more readily with thick films than with thin.

The discontinuity of films of thickness *below* that needed to produce maximum air-passivity seems to be due to quite different causes. At first, it might be thought that it is the consequence of a limited velocity of oxidation, but experiments on film formation in air at the ordinary temperature do not support this view. Several specimens of iron were quickly ground with the carborundum disc, held in air for a definite time, and plunged into iodine. Blank experiments were made with specimens ground under the surface of iodine; these produced no flakes, except for a very small quantity which probably came from the edges of the specimens—places difficult to grind satisfactorily under these conditions. But exposure to air even for so short a time as 8 secs. produced a large crop of flakes which, although ragged and shrivelled, must have occupied a considerable fraction of the whole surface. Exposure to air for longer periods (11, 22, 43, 165 secs.; 5, 10, 20 mins.) gave flakes which became less ragged as the exposure increased. It would appear that the surface oxidation of iron at low temperatures is quite rapid, and the non-protective character of the films in the early stages is due to some other cause.

A further series of experiments showed that the time required

to produce effective air-passivity to copper nitrate solution increased with the coarseness of the abrasive used to prepare the surface. Strips of iron were ground with emery paper of six different grades, and at definite intervals drops of $M/20$-copper nitrate solution were placed on them. The finest-ground strip became unaffected by the copper salt within a few minutes; that ground with the coarsest paper required some hours. No definite "periods of passivation" can be stated, since, during the transition from the active to the passive state, copper-deposition becomes confined to a limited number of points (evidently gaps in the film), and these points gradually become more and more sparsely distributed as the time goes on. During the transition period, therefore, some of the drops on a strip will show copper deposition and others none; a similar lack of reproducibility has been noticed by McCulloch (*Trans. Amer. Electrochem. Soc.*, 1926, **50**, 197), who has found that large pieces of "passive" iron are more liable to fail than small pieces, no doubt because there is a greater probability of a discontinuity occurring somewhere in the film when a large portion is being tested.

The important effect of the abrasive on the time needed for passivity suggests that the cause of local failure of the films produced by air in the early stages of oxidation is due to the internal stresses left by the grinding. A cold-worked metal is necessarily subjected, in different parts, to tensile and compressional stresses; normally the tensile stresses are in equilibrium with the compressional stresses, but if the outer surface undergoes removal or chemical alteration, this equilibrium is destroyed, as shown by Heyn (*J. Inst. Metals*, 1914, **12**, 3) and by Hatfield and Thirkell (*ibid.*, 1919, **22**, 67). When, therefore, the surface layers of cold-ground iron become converted into oxide, forces will at once become available to produce cracking in the films first formed, and although fresh oxidation will keep "repairing" the cracks, cracking will continue until the internal stresses are sufficiently diminished. This will occur quickly if the iron has been ground with fine abrasive, but will require a long time if it has been ground with coarse abrasive, thus explaining completely the observed facts.

It seems possible that the thickening of the film with time may be due rather to the passage of oxygen through the continually opening cracks than to diffusion through the substance of the film itself, diffusion through a solid being a slow process at the ordinary temperature; this would provide an explanation of the variation of the film thickness from place to place. If this explanation is correct, we may expect to find that coarse-ground iron develops films of a greater thickness than fine-ground iron. An actual study of the films from iron ground with six grades of emery confirms this

expectation in a noteworthy manner, the films coming from the iron ground with the finest emery having at the most only one-quarter of the thickness of those derived from iron ground with the coarsest emery, and probably very much less. Measurement of the thinnest films is very difficult, as they contain much opaque residual iron, and the film (which seems almost incapable of existing without support) tends to shrivel around the places where this stronger supporting material is present.

When drops of $M/20$-copper nitrate are placed on specimens of iron which have previously been exposed to air for sufficient time to acquire passivity, no copper is deposited, but a sequence of interference tints slowly appears, indicating a film-thickening. This is another example of the general principle that agencies which tend to cause a film to break down may, under less favourable conditions, simply cause it to thicken. The sequence of colours indicates that the film reaches its greatest thickness at the drop-edges (the usual seat of a breakdown), and becomes continually thinner as the centre of the drop is approached; this is confirmed by converting the film, which consists of ferric oxide, *in situ* into Prussian-blue. A greater final thickness is reached, *ceteris paribus*, on coarse-ground iron than on fine-ground iron, no doubt because the initial thickness is greater when a coarse abrasive has been used.

Films produced by Potassium Chromate.—When electrolytic iron is ground in air and then placed in a solution of potassium chromate, there will usually be the beginnings of an oxide film on the metal before immersion, as a result of oxidation during grinding. As a rule, however, the metal will not be passive towards copper nitrate when it enters the solution, but it gradually acquires passivity through the action of the chromate.

Pieces of electrolytic iron were ground with emery, and at once placed in potassium chromate solution in a thermostat for definite times. The films were then removed with iodine, and studied. A "blank" was performed with metal which had been ground in air like the others, but not immersed in chromate. The flakes from the "blank" (due simply to air exposure during grinding at a temperature unavoidably raised slightly through friction) were of the ragged, shrivelling type characteristic of a discontinuous film, but gradual lengthening of the chromate treatment rendered the flakes less ragged and smaller. The aspect of the metal left after the flakes had been removed by iodine also suggested that the film became more nearly continuous with the immersion in chromate. In the blank, the metal was completely corroded away by the iodine over a large area, but as the chromate exposure was increased the area suffering perforation gradually lessened.

The main function of the chromate, in the case of electrolytic iron, is clearly to repair the discontinuities in the oxide film which had already commenced to grow during the grinding in air, but in addition there is some evidence that the chromate causes thickening of the film. Preparations of flakes were obtained from iron which had been ground with fine emery flour and immersed in *M*-potassium chromate for 4, 8, 16, 32, 128, and 256 mins., respectively, at 11·4°, and the thickness of the flakes was measured; a similar study was made of flakes separated from iron ground with coarse emery. The films obtained from every specimen showed the usual variation of thickness, the thickest flakes being generally 1½—2 times as thick as the thinnest. But there seemed little doubt that the average thickness of "typical" flakes increased somewhat with the time of exposure to chromate solution; the thickening, however, became too slow to be followed when the thickness of typical flakes reached a value about 85—90% of that obtained from iron heat-tinted to the commencement of the first-order yellow; at this stage, the film still contained thinner places (70% of the thickness of the incipient yellow) whilst individual flakes already showed a thickness which, if continuous over the whole surface, would have produced a visible yellow colour. It is not surprising, therefore, that a prolonged exposure to chromate solution can actually confer a yellow tint. Two years ago, the author (*J. Soc. Chem. Ind.*, 1925, **44**, 163T) showed that samples of commercial iron placed in potassium chromate solution for 3 weeks acquired a slight, permanent, yellow tint, whilst similar specimens placed in chromate–chloride mixtures developed yellow, mauve-red, and blue patches around the points of breakdown; the colour sequence indicated a gradual thickening of the film as the site of corrosion was approached, a phenomenon exactly analogous to the variation of thickness recognised at a lower range in the present research. Exposure to air for similar periods did not cause tinting.

Attention must be directed to one difference in the behaviour of continuous and discontinuous films. When a piece of iron, rendered passive by long immersion in potassium chromate solution, is placed in iodine for a sufficient time to loosen the skin, the specimen can be withdrawn with the film still clinging to the metal, although a layer of liquid is present between the film and metal. On gently agitating the specimen with clean water, the film comes off in quite large flakes. If, however, a freshly ground piece of iron is placed in iodine, no film is found on the metal when it is withdrawn, for any rudiments of a film produced by air-treatment during grinding have already passed away into the iodine solution, whence they can afterwards be recovered by the usual settling process.

Electrolytic iron is rendered passive by dry air as readily as by potassium chromate solution. Thus, two specimens of electrolytic iron were treated, one in dry air and the other in *M*-potassium chromate solution, for 22 hours; they were then both quite passive towards *M*/20-copper nitrate and remained quite unaffected in that solution for 13 days; even after 8 weeks, they were both bright and free from copper, although there was a little flocculating rust at the bottom of the vessels. Steel (C, 0·18; Mn, 0·56; Si, 0·04; S, 0·047; P, 0·028; Ni, 0·10%) behaved differently, however: a sample exposed as above to air broke down in *M*/20-copper nitrate within 4 minutes, copper being deposited freely; a sample treated in chromate survived for 20 minutes. Here one must consider the effect of couples set up between the iron (as anode) and cementite (as cathode); electrochemical action of the chromate will necessarily tend to build an oxide film over the anodic area, which must continue until the whole surface becomes equipotential and current ceases to flow; in that condition, the surface is likely to be equipotential in copper nitrate also. There is no *a priori* reason to suppose that exposure to dry air should bring about a surface which would be equipotential in copper nitrate solution. Hence the advantage of obtaining passivity with an electrolyte, such as potassium chromate, is obvious.

Effect of Chlorides on Passive Iron.—The well-known action of chlorides in dispelling passivity is capable of two different explanations: (1) Mere immersion in chlorides may be supposed to loosen or peptise the film, quite independently of the passage of electric current; (2) when passive iron is made an anode, the discharged chlorine ions may be capable of passing through the protective skin, producing corrosion of the metal below and so rendering the skin loose and non-protective. If the first explanation is correct, mere immersion in a chloride solution—under conditions which would preclude the existence of an *E.M.F.* between different parts of the metal—should render passive iron active; if the second explanation is right, the iron should remain passive.

Several experiments were performed to test this point. Discs of electrolytic iron were "whirled" in *M*/20-potassium chromate solution for periods of 30—60 min., thoroughly washed, and then "whirled" for a similar period in sodium chloride solutions (*N*, *N*/10, and *N*/20, in different experiments); for this purpose, the "eccentric whirler," designed to minimise the *E.M.F.*'s due to differential aëration, was employed (Evans, "Corrosion of Metals," 1926, p. 108). After whirling, the discs were taken out, washed, and dried. Spots of rust, apparently marking the site of pores relatively inaccessible to dissolved oxygen, were present on some

discs, but in all cases there were large areas still bright and unchanged; many specimens—apparently those most free from pores—were practically free from rust spots. When drops of $M/20$-copper nitrate solution were applied to the rust-free areas, the metal was found in every case still to be passive, suggesting that the first explanation is wrong. Other experiments at 95° also pointed to the fact that mere immersion in a chloride solution without the passage of current does not dispel passivity. On the other hand, under conditions where the anodic discharge of chlorine ions is possible, chlorides render the iron capable of attack. Iron discs, after the whirling in potassium chromate, suffered rapid attack when made the anode in $N/10$-sodium chloride solution, an *E.M.F.* being applied from an external cell. Again, they were blackened within a minute by contact with $M/20$-copper chloride solution, the replacement of iron by copper being in effect equivalent to anodic attack; they also suffered rusting when drops of $N/10$-sodium chloride were placed on the surface, the *E.M.F.* in the latter case being attributable to differential aëration. These facts indicate that the second explanation represents the more important cause of the activating influence of chlorides.

A study of the anodic attack of previously passive iron in a chloride solution supports this view. Specimens of iron which had been ground with FF emery paper were whirled in $M/20$-potassium chromate, then washed, dried, and subjected (without trimming of the edges) to anodic treatment in $N/10$-sodium chloride solution. At numerous points, dark spots appeared, situated mainly at the parts least accessible to oxygen; they were, for instance, arranged along the grooves left by the grinding and were clustered more closely near the bottom of the electrode than near the water line; along the water line itself, however, there was a row of closely-arranged spots (rather smaller than the others), and grey patches also extended along the edges of the electrode. The whole appearance suggested that at certain points chlorine ions had pierced the skin, producing corrosion below it, and that the skin had been undermined and loosened around these points, the areas thus affected gradually spreading outwards until they met one another. Steel containing chromium, which shows efficient "air-passivity," behaved in an analogous manner. A "stainless steel" knife-blade anodically treated in $N/20$-potassium chloride solution was corroded away entirely around the edges. In the centre, corrosion occurred in circular spots; at many of these spots the blade became completely perforated, with marked undercutting of the surface of the surrounding steel, although between the spots in question the surface remained quite uncorroded.

One question still remains unanswered: Do the chlorine ions themselves perforate the skin, or do they pass through holes which already exist in the skin but which are impervious to other ions? By reason of size alone, chlorine ions might be expected to pass through pores impermeable to polyatomic ions, although our knowledge of osmotic phenomena shows that size is by no means the only factor which influences selective permeability. There is at present no convincing evidence of penetration through pre-existing pores, but the author is disposed to believe that such pores do play a considerable part in the breakdown.

Water-line Attack on Passive Metal.—Many earlier investigators have noted that a passive anode often suffers a slow dissolution, although only a small fraction of the current passing is concerned in corrosion, the remainder being devoted to the production of oxygen. In the present experiments, it was observed that this slow dissolution is mainly due to attack along the water line. A strip of electrolytic iron, 0·8 mm. broad, was subjected to anodic treatment in *N*-potassium sulphate; the cathode was a large iron plate, and the two electrodes were joined to a 6-volt accumulator before immersion in the liquid. The anode was introduced to a depth of only 3 mm., producing instantaneously a high local current density, so as to cause immediate passivity. A vigorous evolution of oxygen was observed over the immersed surface; along the water line, however, the metal was quickly eaten away, leading to perforation; after 37 mins., complete severance occurred at this level, and the lower part of the electrode—still almost uncorroded—fell to the bottom of the vessel. Several other experiments gave similar results.

With air-passive materials, anodic attack at the water line was sometimes very marked. A plate of "staybrite" steel (containing Cr, 18; Ni, 8%) was made the anode in *N*/10-sodium chloride at an average *C.D.* of about 50 milliamps./cm.^{2}. At first, it appeared to act as an inert electrode, oxygen being freely evolved, with a little chlorine. After 15 mins., however, the solution was seen to be turning yellow, and black points appeared at the water level, gradually extending to form a continuous black line. After 18 hours, the immersed portion was still practically uncorroded, but along the water level the corrosion had burrowed deep into the metal, with marked undercutting of the resistant surface layers.

Water-line attack is a marked characteristic of the passive state. The application of an external *E.M.F.* is unnecessary, for it can be produced by simple immersion in iodine solution. Previous work (*J. Soc. Chem. Ind.*, 1925, **44**, 163T) had shown that iron immersed in a chromate–chloride solution suffers intense attack along the water level, although in a chloride solution free from chromate the

zone close to the water line is much *less* attacked than the part lower down; in the case of an air-passive material, the attack by a chloride solution occurs at the water line even in the absence of chromates (Stowell, Congress of Chemists, 1926). The suggestion made in previous papers—that the protective film tends at the water line to cling to the gas–liquid instead of the metal–liquid interface, thus initiating a breakdown—explains all the phenomena observed in the present research. It is not claimed that all cases of water-line corrosion are produced in this way; no doubt there are different causes for the special attack upon this region (Hedges, J., 1926, 831; Evans, *J. Soc. Chem. Ind.*, 1924, **43**, 127T; 1925, **44**, 163T; J., 1925, **127**, 2484). Indeed the term "water-line corrosion" has been used to cover many distinct phenomena, some of which do not occur strictly at the water level itself, but just above or just below it.

Action of Nitric Acid on Electrolytic Iron.—Although diluted nitric acid (*e.g.*, *d* 1·2) acts rapidly on electrolytic iron, the concentrated acid (*d* 1·4) was found to have little action. The liquid became yellow along the metal surface, and a few bubbles of gas were produced, but after about 2 mins. all reaction ceased, and the metal could be kept totally immersed in the acid for hours without change. If the acid was then poured off and the specimen quickly washed, the metal was usually found to be passive towards *M*/20-copper nitrate solution, although occasionally a specimen became covered with copper rapidly, indicating that the passivity produced by nitric acid may break down spontaneously. The specimens showed no resistance to iodine solution.

When pieces of electrolytic iron were dipped below acid of *d* 1·4, then taken out and allowed to drain, after some seconds a violent reaction would start quite suddenly at some point (usually at the top of the wetted area), and travel downwards rapidly until the whole area was evolving bubbles. Soon the reaction would die away, since the acid adhering to the strip became exhausted, and if the strip was then dipped again in acid, and moved about, the brown corrosion-product quickly dissolved away, revealing the bright metallic surface, which appeared quiescent. The spontaneous breakdown of the passivity on removing the metal from the liquid is easily understood, since drainage must soon bring the air–liquid interface close to the metal–liquid interface. The rapid transmission of the reaction downwards from the point of breakdown is perhaps partly due to an undermining of a protective film, but is probably largely connected with the fact that one of the products of the action, *viz.*, water, is known to stimulate the attack. Any reaction in which gaseous oxides of nitrogen are expelled must

increase the ratio $H_2O : N_2O_5$ in the residual liquid, and thus will increase the velocity of the change. Perhaps the rise of temperature, and the passage of electric currents between the active and the passive regions as suggested by Heathcote (*J. Soc. Chem. Ind.*, 1907, **26**, 899) and Lillie (*J. Gen. Physiol.*, 1920, **5**, 107, 129), may also aid the transmission. Numerous observations support the view that one of the corrosion products is, in effect, a catalyst. When a strip wetted with nitric acid was allowed to drain until reaction had just started at a point, and was then plunged into nitric acid with sufficient motion to dissipate the corrosion products in the acid, the transmission ceased and the whole became quiescent; if, on the other hand, the reacting strip was introduced gently into the acid, so that corrosion products could accumulate, the reaction became violent at the water level, causing the strip to be eaten right through, and the lower part, which was usually quiescent, would fall to the bottom of the vessel within a minute. Heathcote's observation, that activity spreads downwards more easily than it spreads upwards, also receives an explanation if we assume that the heavy mixture of corrosion products contains a catalyst.

Of the other products of reaction, nitric oxide, nitrogen peroxide, nitrous acid, and ferric nitrate do not appear to have any marked effect in initiating attack. Nitric acid (*d* 1·4), to which either solid potassium nitrite or ferric nitrate has been added, does not act on electrolytic iron introduced into it. Indeed, ferric nitrate, the final reaction product, has been stated by Ramann (*Ber.*, 1881, **14**, 1430) to favour passivity, and this may be the explanation of the fact that intermediate concentrations of nitric acid can produce either corrosion or passivity according to the procedure employed. For instance, nitric acid (*d* 1·32) caused rapid evolution of gases when an iron strip was introduced into it, but if the strip was at once taken out of the acid and, after the evolution of gas had ceased, was then replaced, the whole remained quiescent, the ferric nitrate having produced passivity. Premature replacement of the strip while still reacting led to rapid attack, causing complete severance at the water level.

The ineffective character of the passivity produced by nitric acid renders the investigation of the protective film by the iodine method difficult, but the general analogy between the passivity produced by this and other methods suggests that nitric acid gives rise to a film which tends to break down spontaneously. It is often stated that no oxide of iron exists possessing the requisite properties. Heathcote's work on the rate of dissolution of *powdered* iron oxides by nitric acid rather supports that view. It seemed, however, advisable to perform experiments on the oxide as a *film*, rather than

as a powder. Accordingly, strips of electrolytic iron were heated at one end so as to give the usual zones of interference colours due to oxide films, the unheated end remaining untinted. When they were placed in nitric acid (*d* 1·4) no change was observed in the colours even after 3½ hours at 23°; had the acid possessed a rapid solvent action on the oxide responsible for the colours, the tints would have disappeared, or at least altered, in the manner produced in a few seconds by cathodic treatment in dilute hydrochloric acid (compare Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 228). When the experiment was repeated with acid of *d* 1·2, the iron was violently attacked at the untinted end; after this end had been completely eaten away, the acid commenced to corrode the iron below the film at the tinted end, causing it to peel off in ragged, microscopic flakes, similar to those produced by the iodine method; the flakes remained undissolved after all the metal had disappeared. A similar peeling could be produced by concentrated acid when 6 days were allowed; in this case, there was practically no formation of bubbles, and the film was obtained in relatively large, transparent flakes. Evidently it is untrue to say that no oxide of iron is capable of resisting the acid to the required extent.

There are many indications that the action of nitric acid is actually capable of producing a film on the metal. In many of the experiments on the action of diluted nitric acid on iron, it was noticed that where the red fumes produced in the reaction swept up over the surface of the iron above the water level, the usual sequence of tints (yellow, reddish-mauve, blue, etc.) was produced, indicating the presence of a film. The very fact that the film had reached visible thickness showed that the physical character was unsuitable to give protection, and it was not surprising to find that in every case the tinted area was not passive towards copper nitrate. But it seems reasonable to suppose that under slightly different conditions the film would be more continuous and would afford better protection, whilst not reaching the thickness sufficient to produce tints; such conditions probably exist in concentrated nitric acid.

The view has sometimes been expressed that the resistance of commercial iron to nitric acid may be due partly to a film of silica, and it was anticipated that iron with a moderate content of silicon would be rendered passive with especial ease. Experiments on several types of the silicon–iron used in electrical machinery showed, however, that the alloys were not specially resistant to nitric acid; one alloy with 3·5% silicon was completely dissolved by nitric acid (*d* 1·40) under conditions which produced a quiescent state on pure iron. These silicon alloys were kindly provided by the General Electric Company.

Examination of Other Metals.—Aluminium, which had been exposed for 6½ hours to air in a desiccator after grinding, on anodic treatment in *N*/10-sodium chloride left a skeleton containing much opaque residual metal, but also a transparent film, the structure bearing signs of the original grinding; the transparent skin was entirely different from the precipitated hydroxide formed in a different part of the cell (where the cathodic sodium hydroxide met the anodic aluminium chloride) and was clearly residual. The iodine method gave confirmation of these results. Aluminium, when freshly abraded or rendered active by immersion in *N*-sodium hydroxide, was quickly attacked by iodine; after 70 minutes' immersion in *M*/20-potassium chromate, it reacted only very slowly. Undermining of the surface layers gave transparent flakes of oxide containing opaque areas due to residual metal. It should be mentioned that the normally invisible skin present on aluminium which has been heated at 800° had already been isolated by Seligman and Williams (*J. Inst. Metals,* 1920, **23**, 169), whilst Bengough and Sutton (private communication) have lately obtained a transparent scale from aluminium previously subjected to anodic treatment in chromic acid.

Copper, when immersed in a chromate solution, becomes covered with a film thick enough to cause a visible browning; it is not surprising to find that this film causes only a temporary protection against silver nitrate. Strips of copper which had been immersed in *M*/20-potassium chromate solution yielded on anodic treatment a skeleton containing some flakes of transparent cupric oxide, bluish-grey by reflected light, some of which bore traces of the original emery treatment, or were continuous with the surface of flakes of residual metallic copper which themselves bore marks of the grinding. There was evidence that the transparent oxide film lacked mechanical strength, and the whole observation was made difficult by the presence of a very large amount of opaque cuprous oxide, bright red by reflected light—evidently a secondary product.

Russell's electronic view of passivity (*Nature,* 1925, **115**, 455; 1926, **117**, 47) is based largely on the assumption that the phenomenon is confined to a small number of metals possessing certain common features in their sub-atomic structure; undoubtedly the metals which are believed to have the sub-atomic structure in question include those which are easily obtained at will either in the active or in the passive state. There seems, however, no reason to draw a line between such metals and those in which one state is far more stable than the other. On considering the "long" form of the Periodic Table, we see on the extreme left the alkali metals, which, having highly soluble oxides, are unlikely normally

to show passivity. To the right of these we find typical "A group" metals, such as aluminium and tantalum, which for some purposes can be regarded as being almost permanently passive; the oxide film causes remarkable permanence in air in spite of the negative electrode potential. To the right of these again are metals such as iron and nickel, in which both active and passive states are fairly stable, and still further to the right we find the "B group" metals which are normally active, although in several cases (copper and zinc) a fleeting type of passivity can be brought about by treatment with chromates.

Summary and Conclusions.

Passive iron is covered with a film which is too thin to give interference tints but which can be removed and thus rendered visible by dissolving away the metal below it by anodic treatment or by means of iodine. This film is the cause of the passivity; where the film is discontinuous or contains cracks, the iron is active. Chlorides favour the activation of passive iron, because chlorine ions can pass through the skin, and at anodic areas the metal is dissolved away below the membrane, which becomes loosened; mere immersion in a chloride solution, under conditions which preclude the flow of local currents, does not necessarily cause passive iron to become active. The attack on passive iron is often localised at the water level, where the film readily becomes loosened. Nitric acid is an untrustworthy reagent for producing passivity on iron, but the phenomena produced by it are probably to be ascribed to film formation, although in this case a film has not actually been isolated. Passive copper and aluminium are covered with transparent films, which have been obtained in flakes; the behaviour of these metals is in many ways analogous to that of iron, although in copper the passivity is less persistent than in iron, whilst in aluminium it is more persistent.

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CXLI.—*The Structure of Normal Fructose: Crystalline Tetramethyl β-Methylfructoside and Crystalline Tetramethyl Fructose* (1 : 3 : 4 : 5).

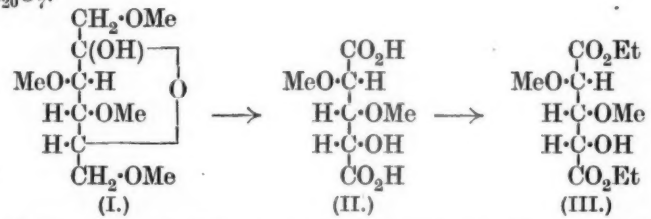
By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and ABRAHAM LEARNER.

THE stable crystalline variety of tetramethyl fructose originally prepared by Purdie and Paul (J., 1907, **91**, 289) has been the subject of a constitutional study by Irvine and Patterson (J., 1922, **121**,

2696), who reached the conclusion that the structural formula of this substance was to be represented as 1 : 3 : 4 : 6-tetramethyl fructose (I). Since it is now recognised that this methylated fructose is structurally similar to ordinary fructose or lævulose, the importance of the allocation of a final constitutional formula to this sugar is evident.

Our reason for instituting an inquiry into the constitution of tetramethyl fructose was that the structure applied to this sugar presented an anomaly when compared with the new structural formulæ we have applied to glucose and other hexoses. The experimental basis for the older formulæ has been shown to be precarious, and an entirely new and fundamental investigation has been necessary in order to place the chemistry of even the simple sugars on a secure basis. Until this was achieved, it was clearly premature to interpret results with any accuracy in the field of the polysaccharides. In the present paper, we have continued our earlier inquiry (Haworth and Hirst, J., 1926, 1858) and have deemed it advisable to scrutinise closely the experimental evidence on which Irvine and Patterson based their conclusions, which have been held to support the butylene oxide formula for fructose, and for stable tetramethyl fructose (I).

These authors reported that in deciding between various competing formulæ which may represent the stable tetramethyl fructose, "the crucial reaction is the formation of dimethoxyhydroxyglutaric acid (II) by the agency of nitric acid." "This oxidation involves the conversion of the $-CH_2 \cdot OMe$ group in the 6 position into CO_2H." It was alleged that the above acid was identified by the isolation and analysis of its diethyl ester (III), which was crystalline (m. p. 86—87°), and its combustion data agreed with the calculated formula, $C_{11}H_{20}O_7$.



(I.) (II.) (III.)

We have repeated this experimental work and have isolated the crystalline oxidation product (m. p. 87—88°) described by Irvine and Patterson. The C and H analysis of this compound agrees with the molecular formula $C_{11}H_{20}O_7$, but other analytical data as well as the properties of the compound are not consistent with its identification as diethyl dimethoxyhydroxyglutarate. Thus, the titration of this substance gives results which hardly support its

formulation as a dibasic ester, but are more in harmony with its recognition as a monobasic ester. It must, however, be recorded that the titration of this compound, inasmuch as it is sensitive to alkali, may easily give misleading results. When warmed with dilute alkali, it gave a yellow solution; it also reduced Fehling's solution readily. This behaviour is characteristic and points definitely to the presence of a reducing group in the substance.

We realised that the constitution of Irvine and Patterson's compound, $C_{11}H_{20}O_7$, could not be securely based on analytical evidence alone, although those authors were content to rely merely on combustion figures, remarking that the determination of methoxyl was "not diagnostic." Further study of the properties of the substance was necessary in order to furnish unmistakable reasons for the constitution (IV) which we have already proposed on other grounds (Haworth and Hirst, *loc. cit.*). The new evidence may now be briefly outlined, and it will be observed that we have relied only on crystalline derivatives which have been ultimately related to substances of definitely known structure.

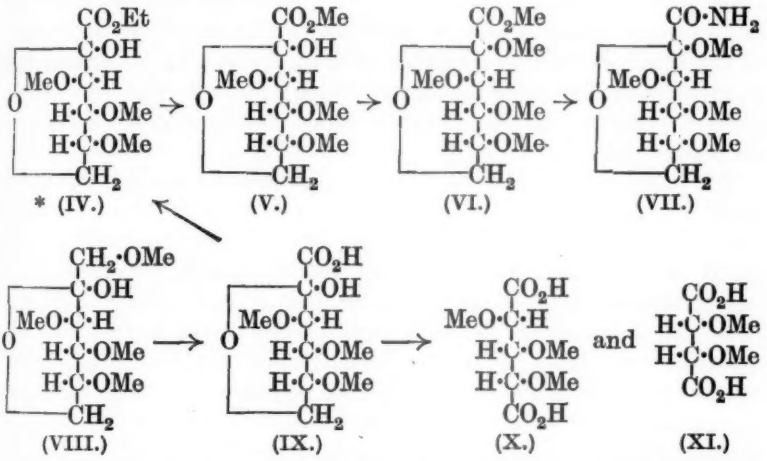
The ethyl ester, $C_{11}H_{20}O_7$, m. p. 87—88° (IV), has been converted directly into the corresponding methyl ester (V), which is crystalline (m. p. 119—120°) and has the molecular formula $C_{10}H_{18}O_7$. The latter had also previously been isolated (Haworth and Hirst, *loc. cit.*) by direct treatment of the acid described by Irvine and Patterson with methyl alcohol and hydrogen chloride. From these facts it is clear that the related acid must be $C_9H_{16}O_7$, and not the dimethoxyhydroxyglutaric acid, $C_7H_{12}O_7$. This methyl ester (m. p. 119—120°), like the ethyl ester (m. p. 87—88°), reduces Fehling's solution actively, but the latter property entirely disappears on the introduction of one additional methyl group by methylation, a procedure which gives rise to a product (VI), m. p. 102°, which is stable to alkali * and is similar in the magnitude of its specific rotation to the original methyl ester, pointing to the retention of the same structural form. This product gives on treatment with methyl-alcoholic ammonia a crystalline amide (VII), m. p. 118—119°, and the nitrogen content and other analytical data

* For this reason, it seems impossible to apply to the methyl ester and the methylated methyl ester the formula of an open-chain ketone such as (A) or (B).

(A) $CO_2Me \cdot CO \cdot [CH \cdot OMe]_3 \cdot CH_2 \cdot OH$ (B) $CO_2Me \cdot CO \cdot [CH \cdot OMe]_3 \cdot CH_2 \cdot OMe$

The cyclic formulæ (V) and (VI) which we have assigned to these products suggest their relation to the monobasic acid obtained by Ohle, Koller, and Berend (*Ber.*, 1925, **58**, 2577) by oxidation of β-fructose-diacetone with permanganate.

of this derivative point to its being the amide of a (methylated) monocarboxylic acid, $C_9H_{16}O_7$. Moreover, we have degraded Irvine and Patterson's ethyl ester (m. p. 87—88°) by further oxidation with nitric acid, and the products isolated were recognised through their crystalline amides. These were (*a*) *d*-arabo-trimethoxyglutaramide, m. p. 227°, and (*b*) inactive dimethoxysuccinamide, m. p. 246°.



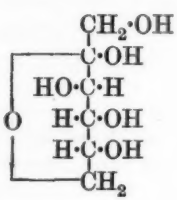
It is evident that *d*-arabo-trimethoxyglutaric acid (X) and *i*-dimethoxysuccinic acid (XI) could not be derived from a primary oxidation product formulated by Irvine and Patterson as in (II) or its ethyl ester as in (III), but the isolation of these acids is consistent with the allocation of the structural formula (IX), or the ethyl ester (IV). For reasons already given in the footnote, an open-chain ketonic formula for the ethyl ester is excluded, and the behaviour of the product both on methylation and on oxidation favours the adoption of the formula (IV). It may be added that the high lævorotation of the substance, which is almost identical with that of the original crystalline tetramethyl fructose, also supports the formulation as a cyclic compound, as does the persistence of the reducing group during treatment with an acid oxidising agent. Had there been present a $>CO$ linking or a terminal $-CH_2{\cdot}OH$ group, neither of these could have survived the treatment with nitric acid. In either event, the evidence from the further oxidation of this product supports our final conclusions ascribing a structure to tetramethyl fructose.

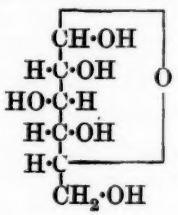
* The oxygen of the ring is not actually directed to the left as shown in these plane formulæ, but is in the same plane as the five carbon atoms of the ring; nor is it implied that the reducing group is necessarily on the right.

In the earlier paper (Haworth and Hirst, *loc. cit.*), it was observed that accompanying the acid $C_9H_{16}O_7$, which we formulate as in (IX), there was also isolated from the oxidation experiments arabo-trimethoxyglutaric acid (X) and *i*-dimethoxysuccinic acid (XI), and it is now made clear that these two acids may be regarded as secondary oxidation products formed by the breakdown of the primary oxidation product (IX) which has been isolated as its ethyl ester (IV) and its methyl ester (V). It would appear that the formation of these secondary products, which alone are of service in determining the ring structure of normal crystalline tetramethyl fructose, eluded the observation of Irvine and Patterson, since they did not examine the liquid esters which were evidently absorbed on porous tile.

The position, therefore, is that had the previous workers ascribed what we now consider to be the correct molecular formula to the primary oxidation product $C_9H_{16}O_7$ or its ethyl ester (IV), this could not in itself have resolved the difficulties attending the determination of the constitution of normal tetramethyl fructose, since the positions of the methoxyl groups would have remained undetermined and also the positions of the oxygen bridge. The cyclic structure of the original hexose appears to be still retained in this oxidation product. Such a result is as unexpected as it is remarkable in the sugar group, inasmuch as during the prolonged treatment with a drastic oxidising agent such as nitric acid (either of concentration *d* 1·2 or *d* 1·42) the first grouping to suffer attack is not the reducing group, which is preserved intact in the primary stage, but the terminal group (1), namely, the $-CH_2\cdot OMe$ group. The grouping in position (6) appears to be unimpaired, the allocation of the carboxyl group to position (6) being rendered impossible by the series of transformations recorded above. These observations serve to explain why normal tetramethyl fructose resists the oxidising action of bromine water and emphasise the stability of the amylene oxide ring, which must now be regarded as a constituent part of this sugar. The parallel behaviour of tetramethyl γ-fructose will be described in a subsequent paper, but here the inter-conversions which have been traced are still more remarkable and furnish an entirely novel conception of the behaviour of sugars.

(XII.)





(XIII.)

In view of the evidence now adduced, supplementing that already furnished (Haworth and Hirst, *loc. cit.*), we consider that the stable crystalline variety of tetramethyl fructose should be indexed as 1 : 3 : 4 : 5-tetramethyl fructose (VIII) containing a 2 : 6-oxide ring. Evidently, ordinary crystalline fructose contains the same structure, and is to be regarded as having also a 2 : 6- or amylene oxide ring (XII), thus bringing normal fructose into line with the revised formula for normal glucose (XIII).

It may also be added that tetramethyl β-methylfructoside, which had previously been described as a colourless liquid, $[\alpha]_D$ — 120·1° in methyl alcohol (Steele, J., 1918, **113**, 257; Irvine and Patterson, J., 1922, **121**, 2696), has now been isolated as a crystalline compound, m. p. 33—34°, $[\alpha]_D$ — 149·1° in water. An improved method of preparation leading to the isolation of this substance in a pure state has been adopted, namely, by subjecting tetra-acetyl β-methylfructoside, as isolated by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216), to the action of alkali and methyl sulphate. The replacement of acetyl groups by methyl groups is completed finally by means of Purdie's reagents.

Experimental.

Preparation of Tetra-acetyl Fructose.—The method of preparation described by Hudson and Brauns (*J. Amer. Chem. Soc.*, 1915, **37**, 2736) was adopted with slight modifications introduced by our colleague, Mr. C. F. Allpress. Finely powdered *d*-fructose (100 g.) was added with constant stirring to 500 c.c. of acetic anhydride, containing 9 g. of zinc chloride, maintained near 0°. After 2 hours, the temperature was kept at 10° for ½ hour, and thereafter at 16° for 2 hours. Then followed the usual treatment with water (500 c.c.), neutralisation with sodium bicarbonate, and extraction of the product with chloroform. The crystalline tetra-acetyl fructose was most conveniently isolated from the dried chloroform extract in the following way. After removal of the solvent by distillation under diminished pressure, an equal volume of ether was added to the warm syrupy residue and, on cooling, the crystalline material separated in a form which could readily be filtered and freed from adhering syrup by washing with ether. Alternatively, the sticky mass of crystals and syrup obtained by Hudson and Braun's method could be extracted with boiling ether, the syrup being thereby removed. Recrystallisation from alcohol gave the pure substance, m. p. 127—129°.

Conversion of Tetra-acetyl Fructose into Tetramethyl β-Methylfructoside.—The tetra-acetyl fructose was treated with methyl iodide and silver oxide to give in quantitative yield tetra-acetyl

methylfructoside, the reagents being used in the proportions given by Irvine and Patterson (*loc. cit.*). The tetra-acetyl methylfructoside was then de-acetylated and methylated in one operation. To 30 g. of tetra-acetyl methylfructoside was added slowly at 50° with very efficient mechanical stirring the theoretical amount of 20% aqueous sodium hydroxide necessary to effect de-acetylation. This was completed in 3 hours. The temperature was then raised to 70° while 76 c.c. of methyl sulphate and 70 g. of sodium hydroxide, dissolved in 140 c.c. of water, were added during a period of 2¼ hours, the concentration of alkali being maintained throughout at about 10%. No darkening in colour took place and after extraction with chloroform in the usual way a pale yellow, mobile syrup was obtained (average yield 13 g.). This on distillation yielded 11 g., b. p. about 103°/0·14 mm., $n_D^{16°}$ 1·4578, $[\alpha]_{5780}$ — 120°; OMe, 55%. Methylation was completed by three successive treatments of the distillate with silver oxide and methyl iodide. This gave, in practically undiminished amount, tetramethyl methylfructoside in the form of a liquid, b. p. 105—106°/0·06 mm., $n_D^{16°}$ 1·4560. After being kept for a few hours, the material began to crystallise spontaneously, and on cooling in an ice-bath a solid mass of hard, flat prisms was obtained. The solid (m. p. 24°) was very soluble even in light petroleum, but by conducting all operations at 0° recrystallisation from this solvent to give pure tetramethyl β-methylfructoside was found to be possible. Four recrystallisations sufficed to raise the m. p. to 33—34°, further treatment being without effect on the m. p. (Found : C, 52·7; H, 8·8; OMe, 60·0. Calc. : C, 52·8; H, 8·8; OMe, 62·0%). The substance showed $[\alpha]_D^{17°}$ — 149·1° in water (c = 3·1) and behaved as a typical glucoside towards Fehling's solution; after hydrolysis with 3% aqueous hydrochloric acid at 95° for 1 hour, crystalline tetramethyl fructose was obtained in excellent yield (after recrystallisation from petroleum, m. p. 98—99°, mixed m. p. with an authentic specimen, 98—99°).

Oxidation of Normal Tetramethyl Fructose.—Crystalline tetramethyl fructose (8 g.) was oxidised with nitric acid (d 1·2) under the conditions described by Irvine and Patterson (*loc. cit.*). Removal of the nitric acid under diminished pressure was followed by esterification of the oxidation product in the usual manner, ethyl alcohol containing 4% of hydrogen chloride being used. After neutralisation with silver carbonate, the solution was evaporated to a syrup, which was dissolved in a mixture of chloroform and ether. Some solid matter was then filtered off, and after the rest of the solvent had been removed addition of light petroleum precipitated an oil which rapidly crystallised. After 15 hours, sufficient ether was added to dissolve adhering syrup and the crystals were

separated by filtration (yield 2·3 g.). Distillation of the syrup remaining in the mother-liquor gave a fraction (bath temp. 170°/10 mm.) which crystallised on cooling to give a further amount of crystalline matter, from which the adhering syrup was removed by absorption in porous tile (total yield of the crystalline product, 3·1 g.). The complete examination of this syrup has already been described in the earlier paper by Haworth and Hirst.

Properties of the Ethyl Ester, $C_{11}H_{20}O_7$.—After recrystallisation from light petroleum the substance showed m. p. 87—88°; $[\alpha]_D$ − 98° ($c = 0{\cdot}928$) in water. It reduced Fehling's solution strongly on warming and was unstable towards hot alkali, giving yellow solutions. For this reason, the titration figures are necessarily inexact and indicate a higher value for CO_2Et than is actually the case. Thus, 0·0917 g. required under standard conditions 4·3 c.c. of $N/10$-sodium hydroxide. This quantity of a substance of formula $C_{11}H_{20}O_7$ calculated as monobasic requires 3·5 c.c.: as dibasic (compare Irvine and Patterson) 7·0 c.c. The formulation as ester of a dibasic acid may therefore be ruled out (Found: C, 49·7; H, 7·7; OMe, 44·9. Calc.: C, 50·0; H, 7·6; OMe, 47·0%).*

Conversion of the Ethyl Ester $C_{11}H_{20}O_7$ *into the Corresponding Methyl Ester.*—The ethyl ester (0·5 g.), dissolved in 15 c.c. of methyl alcohol containing 4% of hydrogen chloride, was gently boiled for 7½ hours. The acid was then neutralised with silver carbonate, and the product isolated in the usual manner. Recrystallisation from ether yielded in all 0·33 g. of a substance identical in all respects with the methyl ester ($C_{10}H_{18}O_7$, m. p. 119°) previously isolated in the course of oxidation experiments with normal tetramethyl fructose. M. p. 119°; mixed m. p. with an authentic specimen 119° (compare Haworth and Hirst, *loc. cit.*).

Preparation of Amide from the Methylated Methyl Ester, $C_{11}H_{20}O_7$ (m. p. 102°).—Owing presumably to complication following on the action of ammonia on the reducing group, it was not found possible to isolate an amide from the methyl ester, $C_{10}H_{18}O_7$. After methylation, however, the non-reducing methylated methyl ester, $C_{11}H_{20}O_7$ (the preparation and properties of which have already been described, Haworth and Hirst, *loc. cit.*), was obtained and readily gave a crystalline amide. A solution of ester in methyl alcohol

* The substance $C_{11}H_{20}O_7$ contains one OEt group and three OMe groups. In such a case, it is convenient for comparative purposes to calculate the OMe percentage for the figures of the Zeisel experiment in the usual way. This is then compared with the theoretical value calculated on the basis of reckoning four OMe groups per molecule of $C_{11}H_{20}O_7$.

(0·3 g. in 2·5 c.c.) was saturated with ammonia at 0° and allowed to remain at room temperature for 4 days. The ammonia and methyl alcohol were then removed under diminished pressure at 25°. The remaining thick syrup crystallised on being rubbed, but the crystals were contaminated with oil. Much of the oil was removed by recrystallisation from a mixture of benzene and petroleum (b. p. 60—80°). Final purification was effected by recrystallisation from light petroleum, needles or long, thin, flat plates being obtained, m. p. 118—119°; $[\alpha]_D$ (approximately) $-137°$ in water ($c = 0·94$) (Found : C, 48·3; H, 7·6; N, 5·5; OMe, 48·4. $C_{10}H_{19}O_6N$ requires C, 48·2; H, 7·6; N, 5·6; OMe, 49·8%).

Oxidation of the Ethyl Ester, $C_{11}H_{20}O_7$ (m. p. 87—88°).—The crystalline ester (1·68 g.) was treated with 22 c.c. of nitric acid (*d* 1·42) at 60°. Oxidation commenced at this temperature, and as the reaction proceeded the temperature was gradually raised to 90—95° and maintained there for 3 hours. The product was isolated as the methyl ester by the usual procedure. On removing the solvent preparatory to purification of the product by distillation under diminished pressure, partial crystallisation took place. The adhering syrup was dissolved in ether and the crystals were separated. They were found to be the methyl ester, $C_{10}H_{18}O_7$ (m. p. 119°), corresponding to the ethyl ester, $C_{11}H_{20}O_7$, used as starting material. Yield 0·53 g.; m. p. and mixed m. p. with authentic specimen 119°. This portion had therefore not undergone oxidation. The syrupy portion of the oxidation product was distilled to give 0·45 g. of colourless syrup, boiling at a bath temperature 160—165°/10 mm.; $n_D^{12°}$ 1·4446. This was dissolved in 3 c.c. of methyl alcohol saturated with ammonia. Rapid deposition of crystalline material began at 20 hours from the start of the experiment. The first crop (0·06 g.) was a mixture (m. p. about 210—215°) which was shown to contain inactive dimethoxysuccinamide by dissolving it in a slight excess of methyl alcohol, nucleating the solution with crystals of the amide in question, and allowing it to evaporate very slowly. The first crystals deposited had the characteristic shape of *i*-dimethoxysuccinamide and gave m. p. 246° (decomp.), and were identified by comparison with genuine *i*-dimethoxysuccinamide. In these comparisons of m.p.'s, it is important that the determinations should be conducted under parallel conditions. By rapid heating, the m. p. can be raised as high as 262°. After 40 hours, a crop of crystals was obtained which, after being washed on the filter with methyl alcohol and ether, proved by comparison with an authentic specimen to be arabo-trimethoxyglutaramide; m. p. 227—228° (decomp.), $[\alpha]_D - 48°$ in water ($c = 0·2$) (Found : OMe, 39·4. Calc. : OMe, 42·2%).

The authors express gratitude to the Department of Scientific and Industrial Research for the award of a maintenance grant to one of them (A. L.).

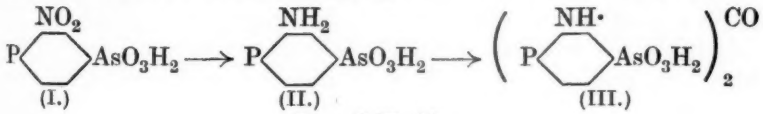
UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, March 28th*, 1927.]

CXLII.—*Trypanocidal Action and Chemical Constitution. Part VI. Amphoteric* s-*Carbamidoarylarsinic Acids.*

By HAROLD KING.

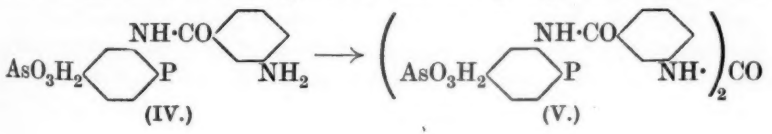
THE physiological action of a drug is primarily a matter of its distribution in the tissues, and among the trypanocidally active aromatic arsinic acids experience has shown that those of an amphoteric nature are the more frequent. This may be attributed to the favourable distribution conferred on substances built somewhat analogously to the simple protein units, the amino-acids. In an earlier communication (Part I; J., 1924, **125**, 2595), it was shown that the *s*-carbamides of some complex aromatic arsinic acids were devoid of trypanocidal action and it was conceivable that this was associated with their non-amphoteric nature. It was therefore deemed of sufficient interest to examine some *s*-carbamidoarsinic acids which still retained a free basic centre. These could be prepared by phosgenation of aminoarsinic acids containing a second basic centre unattacked by phosgene (carbonyl chloride) or by nitration and reduction of *s*-carbamidoarsinic acids. Instances of both classes are recorded below.

As an example of the first type, 4-chloro-3-nitrophenylarsinic acid on treatment with piperidine gave 3-*nitro*-4-*piperidinophenylarsinic acid* (I), which can be reduced to the amino-acid (II). This gives an *acetyl* derivative and also, on phosgenation, a s-*carbamide* (III).



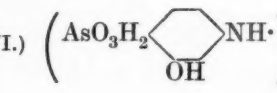
P = $C_5H_{10}N$.

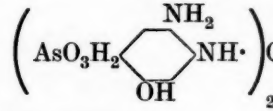
On *m*-nitrobenzoylation, (II) gave 3-m-*nitrobenzamido*-4-*piperidinophenylarsinic acid*, which on reduction gave the 3-m-*aminobenzamido*-derivative (IV); and this on phosgenation gave the



s-*carbamide* (V). These acids were relatively toxic to mice and had no influence on an experimental infection of *Trypanosoma equiperdum* in mice.

As an example of the second type, 4-amino-2-hydroxyphenylarsinic acid on phosgenation gave the s-*carbamido*-derivative (VI), which could be dinitrated to the s-*carbamide* of 5-*nitro*-4-*amino*-2-*hydroxyphenylarsinic acid*. The latter acid on reduction with sodium hyposulphite gave the 4-s-*carbamide* of 4 : 5-*diamino*-2-*hydroxyphenylarsinic acid* (VII). For comparison with the

(VI.) 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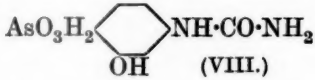
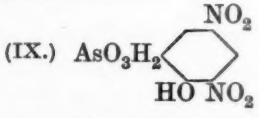
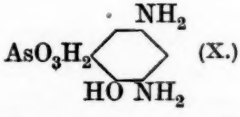

(VIII.)

symmetrical carbamides (VI) and (VII), 2-*hydroxy*-4-*carbamido*-*phenylarsinic acid* (VIII) was prepared by the action of potassium cyanate on 4-amino-2-hydroxyphenylarsinic acid. The maximum dose tolerated by mice expressed in milligrams per gram of mouse, and the minimum curative dose on an experimental infection of *Trypanosoma equiperdum* in mice, of these three carbamides are shown below, *r* signifying the number of days before relapse occurred.

	VI.	VII.	VIII.
Dosis tolerata	0·3	0·8	0·4
Dosis curativa	—	0·8	0·4
	$r = 11$ days.		$r > 30$ days.

The facile way in which the amino-group in 5-nitro-2-aminophenol can be replaced by the arsinic acid group by the Bart–Schmidt reaction (Bauer, *Ber.*, 1915, **48**, 1582; Hewitt and King, J., 1926, 817) suggested its application to picramic acid, which likewise forms an intermediate sparingly soluble quinone-diazide. Here again a good yield of the acid, 3 : 5-dinitro-2-hydroxyphenylarsinic acid (IX), was produced, probably identical with the acid obtained by Benda (*Ber.*, 1911, **44**, 3296) by the nitration of 5-nitro-2-hydroxyphenylarsinic acid.

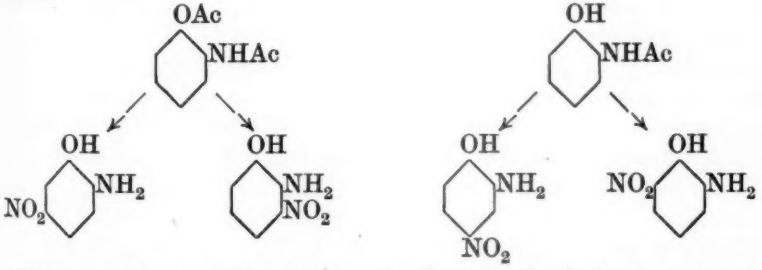
(IX.) 


(X.)

On reduction with sodium hyposulphite it gave a new *diamino*-*hydroxyphenylarsinic acid* (X), of which only two isomerides are known. This proved to be very toxic to mice and was devoid of trypanocidal action.

Nitration of 2- and 4-Aminophenols.

In Part IV of this series (Hewitt and King, *loc. cit.*) it was shown that *N*-acetyl-2-aminophenol or *ONN*-triacetyl-2-aminophenol, when nitrated in sulphuric acid solution with one equivalent of nitric acid, gave mainly 4 : 6-dinitro-2-aminophenol (picramic acid), but that ethenyl-2-aminophenol under similar conditions gave 5- and 4-nitro-2-aminophenols, approximately in the proportion 4 : 1. It has now been shown that *ON*-diacetyl-2-aminophenol in sulphuric acid also nitrates with production of a large proportion of picramic acid and a small proportion of 4-nitro-2-aminophenol. Meldola and Wechsler (P., 1900, **16**, 180) showed that nitration of *ON*-diacetyl-2-aminophenol by fuming nitric acid gave solely 4 : 6-dinitro-2-aminophenol, which they oriented by conversion into 2-chloro-4 : 6-dinitrophenol. This constitution has been confirmed by other means in the present communication, such confirmation being necessary since Ingold and Ingold (J., 1926, 1321), in repeating the earlier work of Meldola, Woolcott, and Wray (J., 1896, **69**, 1330), ascribed the constitution 3 : 5-dinitro-2-aminophenol to this substance, as it was deemed to be in agreement with their results on the mononitration of *ON*-diacetyl-2-aminophenol in acetic anhydride solution. The latter nitration, which leads to the formation of 3- and 5-nitro-2-aminophenols, is of considerable interest, because it has now been shown that under exactly parallel conditions *N*-acetyl-2-aminophenol gives good yields of the other two isomerides —4- and 6-nitro-2-aminophenols—and a small proportion of picramic acid.



These results, at first sight somewhat involved, bear a simple interpretation, since it has been found that *O*-acetyl is hydrolysed to hydroxyl when *ON*-diacetyl-2-aminophenol is dissolved in cold concentrated sulphuric acid and that, although *ON*-diacetyl-2-aminophenol is moderately stable in concentrated nitric acid at − 5°, when nitration has taken place the products have the hydroxyl group free, pointing to immediate nitration after hydrolysis. In either case, solution in sulphuric acid or nitric acid, if hydrolysis precedes nitration the results are consistent.

The apparent nitration of mono-, di-, or tri-acetyl-2-aminophenol in sulphuric acid or of *ON*-diacetyl-2-aminophenol in fuming nitric acid is therefore really the nitration of *N*-acetyl-2-aminophenol and in each case, whether the solvent be sulphuric acid, nitric acid, or acetic anhydride, the nitro-groups enter positions ortho or para, or ortho and para, to the hydroxyl group. When the hydrolysis of *O*-acetyl is prevented by use of acetic anhydride, the nitro-groups enter the ortho- or the para-position to the *N*-acetyl group. These results are in complete agreement with the observations of Reverdin and his associates on the nitration of *N*-acetyl-4-aminophenol (Reverdin and Dresel, *Ber.*, 1905, **38**, 1593), *ON*-diacetyl-4-aminophenol (R. and D., *Ber.*, 1904, **37**, 4453; 1905, **38**, 1593), *N*-benzoyl-4-aminophenol (Reverdin and Delétra, *Ber.*, 1906, **39**, 125), and *ON*-dibenzoyl-4-aminophenol (Reverdin and Dresel, *Ber.*, 1904, **37**, 4453; Reverdin and Delétra, *Ber.*, 1906, **39**, 125), where, however, *O*-acetyl and *O*-benzoyl are not hydrolysed prior to nitration by solution in nitric acid, but *O*-benzoyl is hydrolysed prior to nitration by solution in sulphuric acid. The relative orienting powers for nitro-groups as determined for these aminophenols may be conveniently summarised as follows :

2-Aminophenol.	*4-Aminophenol.*
OH > NHAc	OH > NHAc *or* NHBz
NHAc > OAc	NHAc > OAc; NHBz > OBz

The fact that, with the same solvent, acetic anhydride, and the same nitrating agent, nitric acid or acetylnitric acid, *N*-acetyl-2-aminophenol nitrates ortho and para to the hydroxyl group whilst *ON*-diacetyl-2-aminophenol nitrates ortho and para to the *N*-acetyl group is strong evidence in favour of the view that the induced polarity of the benzene molecule is independent of the solvent or nitrating agent as a major influence, and is probably an electromeric phase of the molecule induced by the substitution of the hydroxyl and amino-groups. From this point of view it is not difficult to understand the peculiar nitration of ethenyl-2-aminophenol which gives 5- and 4-nitro-2-aminophenols, there being two induced electromeric phases. That the solvent or nitrating agent is not without influence is shown by the great tendency for N-acetyl-2-aminophenol to become dinitrated in sulphuric acid solution, although but one equivalent of nitric acid be added, whereas in acetic anhydride solution this is a subsidiary phenomenon.

The author is deeply indebted to Miss F. M. Durham and Miss J. Marchal of this Department for the determination of the trypanocidal activities of the substances herein recorded, to Dr. J. Marshall of the Research Laboratories of Messrs. Boots Pure Drug Co. for a

gift of 4-chloro-3-nitrophenylarsinic acid, and to Dr. J. T. Conroy of the United Alkali Co. for a liberal and free supply of phosgene.

EXPERIMENTAL.

3-Nitro-4-piperidinophenylarsinic Acid (I).—4-Chloro-3-nitrophenylarsinic acid (2·81 g.) and excess of piperidine (5·4 c.c.) were boiled together in 20 c.c. of alcohol for 3 hours. The orange-coloured solution was diluted with water, evaporated to a small volume under reduced pressure, and made neutral to Congo-paper. The gum that separated in quantitative yield, and soon crystallised on being rubbed, was dissolved in 60 c.c. of 0·4*N*-ammonia, and excess of calcium chloride solution added; the finely divided *calcium* salt thus obtained was washed, suspended in water, and treated with hydrochloric acid (Congo-paper). The required *acid* (3·0 g.) separated in pale yellow leaflets (Found : As, 22·3. $C_{11}H_{15}O_5N_2As$ requires As, 22·7%). It crystallises from boiling water in laminated leaflets, is readily soluble in hot acetic or warm 90% formic acid, and dissolves in concentrated hydrochloric acid, forming an almost colourless solution. The *barium* salt separates in filmy leaflets when an ammoniacal solution of the acid is boiled with barium chloride.

3-Amino-4-piperidinophenylarsinic Acid (II).—The above-described nitro-acid (14·8 g.) was reduced with ferrous chloride and alkali in the usual manner. The filtrate from the ferric hydroxide and the weakly alkaline extracts thereof were neutralised (Congo-paper), and concentrated under reduced pressure at 50°. The crystalline *amino-acid* (10·3 g.) thus obtained was purified by solution in 50 c.c. of *N*-hydrochloric acid and careful addition of saturated sodium acetate solution till acidity to Congo-paper was removed (yield 75%) (Found : loss at 100°, 6·0. $C_{11}H_{17}O_3N_2As,H_2O$ requires H_2O, 5·7. Found in anhydrous material : As, 25·2. $C_{11}H_{17}O_3N_2As$ requires As, 25·0%). This amino-acid is instantly soluble in excess of *N*-hydrochloric acid, and yields, with nitrite, an orange-brown solution which couples intensely with alkaline β-naphthol. The pure acid readily forms, when the excess of mineral acid in *N*-hydrochloric acid solution is removed by sodium acetate, a *monohydrochloride*, which crystallises in well-formed, clear prisms (Found : Cl, 10·2. $C_{11}H_{17}O_3N_2As,HCl$ requires Cl, 10·5%). In ammoniacal solution, the acid yields a crystalline *calcium* salt, but the *magnesium* and *barium* salts are precipitated only on boiling. The maximum tolerated dose is 0·01 mg. per g. of mouse.

3-Acetamido-4-piperidinophenylarsinic acid was prepared from the foregoing amino-acid by shaking its alkaline solution with excess of acetic anhydride, added in portions. On neutralisation to Congo-

paper, it separated in small prisms. The yield was quantitative (Found : As, 22·4. $C_{13}H_{19}O_4N_2As$ requires As, 21·9%). This acid is sparingly soluble in boiling water, readily soluble in boiling acetic acid, and crystallises therefrom in diamond-shaped plates. It is instantly soluble in 90% formic acid and in *N*-mineral acids. The maximum tolerated dose is 0·03 mg.

3-m-*Nitrobenzamido*-4-*piperidinophenylarsinic Acid*.—Aminopiperidinophenylarsinic acid monohydrate (6·0 g.), dissolved in 90 c.c. of water containing 2 mols. of sodium hydroxide, was shaken for ½ hour with 7·4 g. of *m*-nitrobenzoyl chloride, and at half-hourly intervals two further quantities of 20 c.c. of *N*-sodium hydroxide were added. On the solution being made definitely acid (Congo-paper) the required *acid* separated, as a gum which rapidly crystallised, mixed with nitrobenzoic acid. The latter was removed by ether extraction. The yield was 92%. For analysis, the acid was purified by solution in dilute aqueous alkali and very gradual precipitation of the warm solution with acid (Found : loss at 100°, 7·3. $C_{18}H_{20}O_6N_3As,2H_2O$ requires H_2O, 7·4. Found in anhydrous material : As, 17·1. $C_{18}H_{20}O_6N_3As$ requires As, 16·7%). This acid is readily soluble in boiling acetic acid and crystallises well in spiked rods. It is soluble in concentrated hydrochloric acid, but is precipitated in well-formed, flattened prisms on dilution. In ammoniacal solution, it yields crystalline precipitates of the *calcium* and *barium* salts on addition of the corresponding chlorides.

3-m-*Aminobenzamido*-4-*piperidinophenylarsinic Acid* (IV).—The foregoing nitro-acid (7·3 g.) was reduced with ferrous chloride and alkali, and the ferric hydroxide precipitate extracted with dilute alkali solution. The combined filtrates were neutralised (Congo-paper), a copious, amorphous precipitate separating; from the filtered solution, concentrated under reduced pressure, a crystalline acid separated. This was dissolved in *N*-hydrochloric acid and fractionally precipitated from the hot solution by saturated sodium acetate solution. After removal of much weakly basic, amorphous material, the required *amino-acid* was obtained in poor yield (2·25 g.) (Found : As, 18·2. $C_{18}H_{22}O_4N_3As$ requires As, 17·9%). This amino-acid is extremely readily soluble in *N*-hydrochloric acid and diazotises and couples with alkaline β-naphthol with formation of a red precipitate insoluble in excess of alkali. In hot ammoniacal solution, it yields a *magnesium* salt, narrow plates, and a *barium* salt, clusters of leaflets, on addition of the corresponding chlorides. The maximum tolerated dose is 0·1 mg.

s-*Carbamide* of 3-*Amino*-4-*piperidinophenylarsinic Acid* (III).—Into a solution of the amino-compound (3 g.) in 200 c.c. of water containing 21·2 g. of anhydrous sodium carbonate (20 mols.),

carbonyl chloride was passed until an acid reaction was obtained. The crude arsinic acid was precipitated by adjusting the reaction to faint acidity to Congo-paper. It was recrystallised by solution in 30 c.c. of *N*-ammonia and addition of concentrated hydrochloric acid, separating as a microscopic, white powder (yield 2·9 g.) (Found: loss at 100°, 2·9. $C_{23}H_{32}O_7N_4As_2,H_2O$ requires H_2O, 2·8. Found in the anhydrous acid: As, 23·8. $C_{23}H_{32}O_7N_4As_2$ requires As, 23·9%). This acid is almost insoluble in boiling glacial acetic acid, but dissolves readily on addition of a small proportion of water and then crystallises, on cooling, in microscopic rods. It is readily soluble in 3*N*-hydrochloric acid. The *magnesium* salt crystallises in elongated leaflets from ammoniacal solution containing ammonium chloride. The maximum tolerated dose is 0·075 mg.

s-*Carbamide of* 3-m-*Aminobenzamido*-4-*piperidinophenylarsinic Acid* (V).—Prepared similarly to the preceding one, this *carbamide* was obtained in quantitative yield. It was purified for analysis and physiological testing by dissolving it in 5 volumes of 90% formic acid and adding the solution to 50 volumes of boiling water. On continuing the boiling, the carbamide gradually separated (Found: loss at 100°, 5·8. $C_{37}H_{42}O_9N_6As_2,3H_2O$ requires $3H_2O$, 5·9. Found in the anhydrous acid: As, 17·8. $C_{37}H_{42}O_9N_6As_2$ requires As, 17·4%). This carbamide is soluble in concentrated hydrochloric or formic acid and is precipitated on dilution. It is practically insoluble in boiling glacial acetic acid or 50% formic acid, but its crystalline form may be seen by dissolving it in cold 90% formic acid, adding water until a turbidity is produced, boiling the solution, and continuing the addition of water until the solution is again turbid; on cooling, the carbamide crystallises in microscopic, woolly needles. The amorphous *magnesium*, *calcium*, and *barium* salts are immediately precipitated from dilute ammoniacal solution, and the *sodium* salt is precipitated in amorphous particles by addition of excess of 2*N*-sodium hydroxide to a solution of the sodium salt. The maximum tolerated dose is 0·2 mg.

s-*Carbamide of* 4-*Amino*-2-*hydroxyphenylarsinic Acid* (VI).—The amino-acid (4·7 g. of monohydrate) was phosgenated in the presence of sodium carbonate (10 mols. in 200 c.c. of water) until the reaction was acid. The crystalline precipitate (3·5 g.) was dissolved in dilute ammonia and reprecipitated by acid (yield 3·3 g.) (Found: loss at 100°, 7·6. $C_{13}H_{14}O_9N_2As_2,2H_2O$ requires H_2O, 6·8. Found in anhydrous solid: As, 30·5. $C_{13}H_{14}O_9N_2As_2$ requires As, 30·5%). This carbamide is practically insoluble in boiling acetic or formic acid; it is sparingly soluble in boiling water, and crystallises therefrom in rods. Dilute ammoniacal solutions gave immediate amorphous precipitates with calcium, magnesium, and barium chlorides.

An aqueous or, better, alcoholic solution of the acid gives a port-wine colour on addition of ferric chloride. The maximum tolerated dose is 0·3 mg.

s-*Carbamide of* 5-*Nitro*-4-*amino*-2-*hydroxyphenylarsinic Acid*.—The preceding carbamide (7·0 g.) in 28 c.c. of sulphuric acid was nitrated at 0° with 2·8 g. of nitric acid (*d* 1·42) in 3 c.c. of sulphuric acid. The solution was poured into water, and a yellow, crystalline solid (7·8 g.) slowly separated. When stirred with cold water, this carbamide yields a yellow, opalescent solution. It is readily soluble in boiling water; on cooling, the solution becomes acid to Congo-paper, and gradually becomes limpid with deposition either of the anhydrous *acid*, crystallising in yellow plates, or of the *dihydrate* in fine, yellow needles (Found: loss at 100°, 6·0. $C_{13}H_{12}O_{13}N_4As_2,2H_2O$ requires H_2O, 5·8%). The *magnesium*, *barium*, and *calcium* salts are precipitated amorphous from ammoniacal solution. The *sodium* salt crystallises well and is only moderately easily soluble in water. The *tetra-ammonium* salt is sparingly soluble and crystallises in fine, orange-yellow needles. It is partly hydrolysed by washing with water, as is shown by analysis [Found: loss at 100°, 10·1. $C_{13}H_{12}O_{13}N_4As_2,3\frac{1}{2}NH_3,4H_2O$ requires H_2O, 10·1. Found in the anhydrous salt: volatile NH_3, 8·7; As (Lehmann), 23·3. $C_{13}H_{12}O_{13}N_4As_2,3\frac{1}{2}NH_3$ requires NH_3, 9·3; As, 23·3%].

s-4-*Carbamide of* 4 : 5-*Diamino*-2-*hydroxyphenylarsinic Acid* (VII)—A clear solution of the preceding nitro-compound (1·16 g.) in 12 c.c. of *N*-sodium hydroxide at 0° was treated with 5 g. of sodium hyposulphite, and the external cooling agent simultaneously removed. On stirring for about 2 hours, the precipitated yellow nitro-compound was replaced by the required *amino*-compound. This was collected, dissolved in 11 c.c. of *N*-hydrochloric acid, and precipitated, as an almost white, microcrystalline powder, by addition of sodium acetate (yield 85%) (Found: loss at 100°, 6·9. $C_{13}H_{16}O_9N_4As_2,2H_2O$ requires H_2O, 6·5. Found in dried substance: As, 28·4. $C_{13}H_{16}O_9N_4As_2$ requires As, 28·7%). This amino-acid is readily soluble in dilute mineral acids, but its salts are hydrolysed on dilution. It gives a yellow solution on addition of sodium nitrite but does not couple with alkaline β-naphthol, probably owing to the formation of a soluble diazoimide. The maximum tolerated dose is 0·8 mg.

2-*Hydroxy*-4-*carbamidophenylarsinic Acid* (VIII).—The parent amino-acid (1·35 g.) in 2·5 c.c. of water was treated with 1·74 g. of potassium cyanate (4 mols.); all then passed into solution. After addition of 0·8 c.c. of glacial acetic acid the solution was kept for 24 hours and then made acid (Congo-paper), and the precipitate was

collected (yield 1·25 g.). On careful addition of sodium acetate to the filtrate, 0·15 g. of unchanged amino-acid was recovered (Found: loss at 100°, 3·3. $C_7H_9O_5N_2As,\frac{1}{2}H_2O$ requires H_2O, 3·2. Found in dried substance: As, 27·2. $C_7H_9O_5N_2As$ requires As, 27·2%). This acid is soluble in 66 parts of boiling water and crystallises in fine needles. Its ammoniacal solution gives immediate precipitates of the amorphous *magnesium* and *calcium* salts on addition of the respective chlorides, but the *barium* salt, obtained on boiling, is crystalline. The maximum tolerated dose is 0·4 mg.

3 : 5-*Dinitro*-2-*hydroxyphenylarsinic Acid* (IX).—Picramic acid (10·0 g.) was suspended in 60 c.c. of 3*N*-hydrochloric acid at 0° and diazotised by addition of 3·8 g. of sodium nitrite in 38 c.c. of water. Arsenic trioxide (6·2 g.) in 37·2 c.c. of 2*N*-sodium hydroxide was now added rapidly, and into the still acid solution 2*N*-sodium hydroxide (about 150 c.c.) was run slowly until all the brightly coloured quinone-diazide had disappeared and evolution of nitrogen had ceased. The solution was acidified (Congo-paper) and, after removal of amorphous matter, concentrated at 50°. Two crops (10·15 g. in all) of crude dinitro-acid were obtained which, on two crystallisations from 50 c.c. of boiling water, gave yellow leaflets (yield 8·7 g.), m. p. 244—246° (Benda, *loc. cit.*, gives 237°) (Found: As, 24·7. Calc.: As, 24·3%). This acid, treated with 2*N*-ammonia, gives a sparingly soluble *ammonium* salt, which crystallises from water in needles. The *calcium* and *magnesium* salts are precipitated amorphous from ammoniacal solution, but the *barium* salt is crystalline.

3 : 5-*Diamino*-2-*hydroxyphenylarsinic Acid* (X).—The preceding dinitro-acid (1·0 g.), dissolved in 10 c.c. of *N*-sodium hydroxide at 0°, was treated with 5 g. of sodium hyposulphite all at once, the external bath being simultaneously removed. The temperature rose to about 30° and on continuing the stirring the *diamino*-compound crystallised in long needles (yield 0·5 g.) [Found: As, 30·8 (Carius), 29·7 (Lehmann). $C_6H_9O_4N_2As$ requires As, 30·2%]. This diamino-acid is very soluble in dilute mineral acids and gives a reddish-brown solution on addition of a trace of nitrite. It reduces ammoniacal silver nitrate solution instantaneously and gives a port-wine colour on addition of potassium dichromate solution. The maximum tolerated dose is 0·04 mg.

Nitration of ON-*Diacetyl*-2-*aminophenol*.—(a) *By nitric acid*. Ten g. of the diacetyl compound were nitrated as described by Meldola, Woolcott, and Wray (*loc. cit.*) and Ingold and Ingold (*loc. cit.*). On dilution with ice *N*-acetylpicramic acid was obtained, m. p. 203°, in 63% yield. On crystallisation from much boiling water it separated in soft, yellow needles, m. p. 205—206°. Its identity was

proved by the melting points of its mixture with monoacetylpicramic acid and of mixtures of its acid hydrolytic product with picramic acid and of its diacetylated derivative with *ON*-diacetylpicramic acid. ON-*Diacetylpicramic acid* is readily obtained by boiling picramic or monoacetylpicramic acid with acetic anhydride and a few drops of pyridine. It crystallises from 5 volumes of boiling acetic acid in needles, m. p. 190—191°. *N*-Acetylpicramic acid is obtained by allowing picramic acid to react at room temperature with a small volume of acetic anhydride.

(b) *By nitric acid in sulphuric acid.* Anhydrous *ON*-diacetylaminophenol (9·7 g.) was dissolved at — 5° in 40 c.c. of sulphuric acid and nitrated by the gradual addition of 5 g. of nitric acid (*d* 1·42) mixed with 2·5 c.c. of sulphuric acid. On pouring the solution on ice, 9·0 g. of crude nitration products separated, and ether extraction of the mother-liquor gave 1·1 g. of highly coloured gum. The main crop of solid was hydrolysed by 10% hydrochloric acid and gave, on dilution and partial neutralisation, 3·3 g. of picramic acid. On neutralisation to Congo-paper, the mother-liquor gave 0·9 g. of 4-nitro-2-aminophenol, m. p. 140° (anhydrous) and not depressed by admixture with pure 4-nitro-2-aminophenol. Ether extraction of the final liquors gave 1·05 g., which, on acetylation, gave 1·1 g., m. p. 266°; this, on crystallisation from 45 c.c. of alcohol, gave 0·75 g., melting, alone or mixed with 4-nitro-2-acetamidophenol, at 280°. The aqueous liquors from the acetylation deposited 0·05 g., m. p. 178°, which, on crystallisation from alcohol, gave 4-nitro-*ON*-diacetylaminophenol; this, alone or mixed with a genuine sample of 4-nitrodiacetylaminophenol, melted at 184°. These yields indicate a 66% conversion of the available nitric acid into dinitro-derivative (picramic acid) and a 17·5% conversion into mononitro-derivative.

(c) *By nitric acid in acetic anhydride.* Following Ingold and Ingold (*loc. cit.*), 14·5 g. of diacetyl-2-aminophenol were nitrated in acetic anhydride at 10°. *ON*-Diacetyl-3-nitro-2-aminophenol (1·45 g.) separated in diamond-shaped plates; the product obtained by pouring the mother-liquor into water was fractionally crystallised from alcohol, giving *ON*-diacetyl-5-nitro-2-aminophenol. The 3-nitro-derivative (1·0 g.) was hydrolysed by boiling it with 3*N*-hydrochloric acid and gave, on removal of the acidity to Congo-paper, 0·55 g. of 3-*nitro-2-aminophenol*; this was soluble in 100 parts of boiling water and crystallised in red needles, m. p. 216—217° (Found: C, 46·2; H, 3·9. $C_6H_6O_3N_2$ requires C, 46·7; H, 3·9%). It gave an intense red colour on addition of alkali.

A comparison of the relative colour intensities of 0·2% solutions of 3-, 4-, 5-, and 6-nitro-2-aminophenols in 0·5*N*-sodium

hydroxide by means of the Lovibond tintometer gave the following values :

	3-*Nitro.*	4-*Nitro.*	5-*Nitro.*	6-*Nitro.*
Red	36	16	31	15
Yellow	11	18	14	15

Definite maxima of redness which control the general visible intensity are thus found for the two compounds which are *m*-nitrophenols. It thus appears that the chromophoric character in alkaline solution of the *o*- and *p*-nitroaniline groups may be greater than that of the *o*- and *p*-nitrophenolic groups.

Nitration of N-*Acetyl-2-aminophenol.—By nitric acid in acetic anhydride.* A solution of monoacetyl-2-aminophenol (1·5 g.) in 50 c.c. of acetic anhydride at 80° was cooled to 30°, and nitric acid (0·5 c.c.; *d* 1·5) in 2·5 c.c. of acetic anhydride then slowly added. On cooling, there separated 0·5 g. of 4-nitro-2-acetamidophenol, m. p. 279—280°. In admixture with an authentic specimen and with 5-nitro-2-acetamidophenol, this melted at 279—280° and at 245°, respectively. The mother-liquor, on concentration at 70°, gave no further deposit. It was therefore evaporated twice with water at 50°, the residue hydrolysed by boiling for 1 hour with 3*N*-hydrochloric acid, and the solution neutralised (Congo-paper). The brown solid (0·4 g.), m. p. about 100°, thus obtained was ground with *N*-hydrochloric acid, and water gradually added to dissolve the crystalline hydrochloride. The insoluble red solid (0·05 g.) was picramic acid, m. p. 165°, mixed m. p. with pure picramic acid 167°. The soluble fraction, on neutralisation at 80°, gave 0·35 g. of 6-nitro-2-aminophenol; this crystallised in long, maroon-coloured needles, m. p. 112—113°, and its properties agreed with those described for 6-nitro-2-aminophenol by Benda (*Ber.*, 1914, **47**, 1010), except that it gave a red and not a blue solution when diazotised and added to R-salt; with alkaline β-naphthol, it gave a purple precipitate. The original aqueous liquors were neutralised (litmus), and extracted with ether; this removed 0·25 g. of unchanged 2-aminophenol which, alone or mixed with pure 2-aminophenol, melted at 174°.

Action of Sulphuric Acid on ON-*Diacetyl-2-aminophenol.*—A solution of 1 g. of *ON*-diacetyl-2-aminophenol in 2 c.c. of sulphuric acid at 10—15° was, after 1 hour, diluted with ice; extraction with ether than gave *N*-acetyl-2-aminophenol in almost quantitative yield.

Action of Nitric Acid on ON-*Diacetyl-2-aminophenol at* — 5°.— One g. of diacetylaminophenol was dissolved in a mixture of 4 c.c. of nitric acid (*d* 1·42) and 2 c.c. (*d* 1·5) at — 5° and kept at this temperature for ½ hour. When the solution was mixed with ice,

proved by the melting points of its mixture with monoacetylpicramic acid and of mixtures of its acid hydrolytic product with picramic acid and of its diacetylated derivative with *ON*-diacetylpicramic acid. ON-*Diacetylpicramic acid* is readily obtained by boiling picramic or monoacetylpicramic acid with acetic anhydride and a few drops of pyridine. It crystallises from 5 volumes of boiling acetic acid in needles, m. p. 190—191°. *N*-Acetylpicramic acid is obtained by allowing picramic acid to react at room temperature with a small volume of acetic anhydride.

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Definite maxima of redness which control the general visible intensity are thus found for the two compounds which are *m*-nitrophenols. It thus appears that the chromophoric character in alkaline solution of the *o*- and *p*-nitroaniline groups may be greater than that of the *o*- and *p*-nitrophenolic groups.

Nitration of N-*Acetyl-2-aminophenol.—By nitric acid in acetic anhydride.* A solution of monoacetyl-2-aminophenol (1·5 g.) in 50 c.c. of acetic anhydride at 80° was cooled to 30°, and nitric acid (0·5 c.c.; *d* 1·5) in 2·5 c.c. of acetic anhydride then slowly added. On cooling, there separated 0·5 g. of 4-nitro-2-acetamidophenol, m. p. 279—280°. In admixture with an authentic specimen and with 5-nitro-2-acetamidophenol, this melted at 279—280° and at 245°, respectively. The mother-liquor, on concentration at 70°, gave no further deposit. It was therefore evaporated twice with water at 50°, the residue hydrolysed by boiling for 1 hour with 3*N*-hydrochloric acid, and the solution neutralised (Congo-paper). The brown solid (0·4 g.), m. p. about 100°, thus obtained was ground with *N*-hydrochloric acid, and water gradually added to dissolve the crystalline hydrochloride. The insoluble red solid (0·05 g.) was picramic acid, m. p. 165°, mixed m. p. with pure picramic acid 167°. The soluble fraction, on neutralisation at 80°, gave 0·35 g. of 6-nitro-2-aminophenol; this crystallised in long, maroon-coloured needles, m. p. 112—113°, and its properties agreed with those described for 6-nitro-2-aminophenol by Benda (*Ber.*, 1914, **47**, 1010), except that it gave a red and not a blue solution when diazotised and added to R-salt; with alkaline β-naphthol, it gave a purple precipitate. The original aqueous liquors were neutralised (litmus), and extracted with ether; this removed 0·25 g. of unchanged 2-aminophenol which, alone or mixed with pure 2-aminophenol, melted at 174°.

Action of Sulphuric Acid on ON-*Diacetyl-2-aminophenol.*—A solution of 1 g. of *ON*-diacetyl-2-aminophenol in 2 c.c. of sulphuric acid at 10—15° was, after 1 hour, diluted with ice; extraction with ether than gave *N*-acetyl-2-aminophenol in almost quantitative yield.

Action of Nitric Acid on ON-*Diacetyl-2-aminophenol at* — 5°.— One g. of diacetylaminophenol was dissolved in a mixture of 4 c.c. of nitric acid (*d* 1·42) and 2 c.c. (*d* 1·5) at — 5° and kept at this temperature for ½ hour. When the solution was mixed with ice,

0·5 g. of unchanged diacetyl-2-aminophenol separated; ether extraction of the mother-liquor gave a further 0·15 g. containing traces of nitrated products.

The thanks of the author are due to Mr. W. K. Anslow for help in the preparations and analyses.

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CXLIII.—*The Properties of Conjugated Compounds. Part II. Addition to Butadiene Esters.*

By ERNEST HAROLD FARMER and ALFRED THOMAS HEALEY.

IT has been established that the addition of esters to αβ-unsaturated esters and ketones can take place reversibly in two ways, yielding products of the normal and the abnormal type ·CHX·CH_2·CO and CH_2·CHX·CO [X=$CH(CO_2Et)_2$, etc.], respectively, although generally one type of addition may be favoured to the practical exclusion of the other. The formation of one or other (or both) of the additive products in a given case is dependent on a system of connected equilibria which vary with the experimental conditions but are not greatly affected by the polar condition of the reactants (compare E. H. Ingold, J., 1925, **127**, 469; Cooper, Ingold, and Ingold, J., 1926, 1868). With conjugated esters of the type CH:CH·CH:CH·C:O, however, the possible modes of additive reaction are more numerous. Vorländer, in securing the attachment of the malonic residue at the δ-carbon atom of methyl sorbate (*Annalen*, 1906, **345**, 227), experimentally demonstrated that they are not confined to αβ-addition, and it is possible that attachment of the components of the addendum may occur simultaneously or alternately in two or more ways.

In seeking evidence of the variability or otherwise of addition to butadiene derivatives, the additive properties of sorbic and β-vinylacrylic acids were studied. The addition of methyl sodiomalonate to the esters of these acids has recently been examined by Kohler and Butler (*J. Amer. Chem. Soc.*, 1926, **48**, 1036), who obtained in the respective cases excellent yields of the compounds $(MeO_2C)_2$CH·CHMe·CH:CH·CH_2·CO_2Me (I) and

$(MeO_2C)_2$CH·CH_2·CH:CH·CH_2·CO_2Me (II),

which appeared to be the sole products of addition. Our experiments, carried out before the appearance of Kohler and Butler's paper, gave results concerning the formation and constitution of these compounds in complete agreement with those of the latter authors, and in the case of methyl β-vinylacrylate, particularly, the absence

of any but the minutest traces of a second additive product was readily demonstrable. Further, an examination of (II) showed it to be non-mobile : it neither suffered double-bond displacement by the action of sodium methoxide nor showed any tendency to undergo further condensation with esters like methyl cyanoacetate. Therefore its formation by a process of $\gamma\delta$-addition—a possibility not usually considered but which would be somewhat analogous to the formation of γ-oxalyl derivatives of $\beta\beta$-dimethylacrylic ester (Higginbotham and Lapworth, J., 1923, **123**, 1325)—followed by double-bond displacement is out of the question. The additions are indubitably and completely of $\alpha\delta$-type.

Attempts to obtain a different result by varying the experimental conditions of condensation failed entirely, but the limits of variation with substances so prone to polymerisation as sorbic and β-vinylacrylic esters were necessarily narrow. Attention was therefore directed to the effect of varying the ester-addendum, as, for instance, by alkylation. Few cases of the employment of alkylated malonic and cyanoacetic esters in the Michael reaction are recorded in the literature. Thorpe observed (J., 1900, **77**, 932) that during reaction between ethyl $\beta\beta$-dimethylacrylate and ethyl methylsodiocyanoacetate the addendum appeared to suffer an unusual partition, $CH_3-\!\!-C(CN):C(ONa)\cdot OEt$, leading to the formation of the methylable sodio-derivative of an ester $EtO_2C\cdot CHMe\cdot CMe_2\cdot CH(CN)\cdot CO_2Et$. E. H. Ingold has interpreted the observations of Bone and Sprankling (J., 1899, **75**, 839) concerning the interaction of ethyl ethylsodiomalonate and ethyl α-bromo*iso*butyrate in a manner involving reversible Michael additions, whereby the effect of the alkyl group of the addendum is to favour the abnormal type of $\alpha\beta$-addition. With both sorbic and β-vinylacrylic esters, however, the addition of ethyl methylcyanoacetate, which readily takes place, follows the same course as with ethyl malonate; the esters (III) and (IV) are exclusively produced in the respective cases, the constitutions following from the nature of the ozone degradation products as shown below.

$$\begin{array}{l}\mathrm{CHMe\cdot CH{:}CH\cdot CH_2\cdot CO_2Me} \xrightarrow{O_3} \\ \mathrm{CMe(CN)\cdot CO_2Et}\end{array} \quad \mathrm{CH_3\cdot CHO} + \begin{array}{l}\mathrm{CHMe\cdot CO_2H} \\ \mathrm{CMe(CN)\cdot CO_2Et}\end{array} \longrightarrow \begin{array}{l}\mathrm{CHMe\cdot CO_2H} \\ \mathrm{CHMe\cdot CO_2H}\end{array}$$

(III.) *cis* and *trans*

$$\begin{array}{l}\mathrm{CH_2\cdot CH{:}CH\cdot CH_2\cdot CO_2Me} \xrightarrow{O_3} \\ \mathrm{CMe(CN)\cdot CO_2Et}\end{array} \quad \mathrm{CH_3\cdot CHO} + \begin{array}{l}\mathrm{CH_2\cdot CO_2H} \\ \mathrm{CMe(CN)\cdot CO_2Et}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2\cdot CO_2H} \\ \mathrm{CHMe\cdot CO_2H}\end{array}$$

(IV.)

Indeed in no experiment could any divergence from the type of ester-addition be observed, and in particular there is little doubt

of the entire absence of αβ-products. Consequently, any representation such as that of Kohler and Butler (1 : 4-additive product $\rightleftharpoons CH_2{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me + Na[CH(CO_2Me)_2] \rightleftharpoons$ 1 : 6-additive product) is at present purely speculative. In view of the foregoing results, the observation that ethyl methyl*cyclo*hexenylidenecyanoacetate (V) under Guareschi's conditions adds on the components of

(V.) $CH_2<\begin{matrix}CMe{=}CH\\CH_2{\cdot}CH_2\end{matrix}>C{:}C(CN){\cdot}CO_2Et$ $CH_3{\cdot}CH{:}CH{\cdot}CH{:}C(CO_2Et)_2$ (VI.)

ethyl cyanoacetate at the αβ-carbon atoms (Farmer and Ross, J., 1926, 1577) is of interest; this substance may be regarded as a substituted sorbic ester in which both spatial and polar conditions are modified—a modification which causes complete change of additive mode. With the α-carboxysorbic ester (VI) addition of esters could not be secured.

It was shown by Auwers and Heyna (*Annalen*, 1923, **434**, 140) that sorbic acid adds on bromine at the γδ-double bond. β-Vinylacrylic acid behaves similarly. The crude dibromide consisted of a mixture of crystalline and liquid material, each portion of which yielded with diethylamine a crystalline bromovinylacrylic acid. The identity or otherwise of these two products could not be satisfactorily determined, since both polymerised on heating and neither could be satisfactorily reduced. The bromination product was, however, constitutionally homogeneous, both solid and liquid portions yielding acraldehyde dibromide (identified by conversion into α-bromoacraldehyde) and oxalic acid. No trace of material derived by αβ- or βγ-addition could be isolated.

Experimental.

A. Derivatives of β-Vinylacrylic and Sorbic Acids.

β-Vinylacrylic acid, prepared by Doebner's method (*Ber.*, 1902, **35**, 1137), was purified by solution in ether and extraction with dilute aqueous sodium carbonate. The acid obtained by re-extracting the alkaline liquid was drained on porous tiles and recrystallised from petroleum. It formed colourless, prismatic needles, m. p. 80° (Doebner, m. p. 80°; Kohler and Butler, m. p. 72°).

The *dibromide* was obtained in the usual way, carbon disulphide being used as diluent. The crude product, thoroughly freed from carbon disulphide, partly solidified when cooled in an ice–salt mixture. The semi-solid mass was spread on porous tiles; these absorbed the oily matter, leaving a solid which separated from petroleum in tufts of colourless needles, m. p. 47° (Found : Br, 61·55. $C_5H_6O_2Br_2$ requires Br, 62·0%). The *methyl* ester, obtained by the action of methyl alcohol and sulphuric acid on the solid dibromide,

was a pale yellow oil, b. p. 136°/10 mm. (Found: Br, 58·6. $C_6H_8O_2Br_2$ requires Br, 58·8%).

Extraction of the porous tiles with ether yielded a brown oil (about one-fifth of the total product) from which no further solid matter could be obtained. From this dibromo-acid (Found: Br, 61·6%), which was examined separately, the *methyl* ester was obtained as a pale yellow oil, b. p. 134—136°/12 mm. (Found: Br, 59·1%).

Bromo-β-vinylacrylic Acid.—The solid dibromide (10 g.), dissolved in absolute ether (150 c.c.), was gradually treated with an ethereal solution of diethylamine (8 g.) at 0°. Diethylamine hydrobromide separated rapidly; when separation had ended, the ethereal liquor was filtered, agitated several times with dilute sulphuric acid, and finally dried. Removal of the solvent yielded an acid which crystallised from benzene–petroleum in long, colourless needles (Found: Br, 44·9. $C_5H_5O_2Br$ requires Br, 45·2%). When this substance was heated, it changed without melting or evident degradation to a yellow, apparently amorphous, solid which gradually darkened in colour as the temperature rose. A similar yellow solid, doubtless a polymeride of bromovinylacrylic acid, was obtained when boiling pyridine was employed in place of diethylamine. Pure crystalline bromovinylacrylic acid could not be kept; invariably it changed, in less than 2 days, to a brown, amorphous mass. The *methyl* ester, obtained in similar fashion from the ester of the solid portion of the dibromide (above), was a pale yellow oil which solidified on cooling to 0° (m. p. about 10°), but polymerised to a thick jelly on standing for 2 hours at room temperature.

Removal of hydrogen bromide from the liquid portion of the dibromide (using ethereal diethylamine) yielded a bromovinylacrylic acid which crystallised from benzene–petroleum in colourless plates (Found: Br, 44·9%). When heated, this acid behaved like the above described monobromo-acid; when allowed to stand, the crystalline form was gradually lost, the change becoming marked after 7—8 days. The *methyl* ester obtained in a similar way from the ester of the liquid portion of the dibromide (above) was a yellow oil, b. p. 95—98°/16 mm., which polymerised within 8 hours of distillation (Found: Br, 41·7. $C_6H_7O_2Br$ requires Br, 41·9%). Attempts to establish the identity of the two specimens of bromovinylacrylic acid did not succeed; reduction to vinylacrylic acid could not be effected.

Sorbic Acid Dibromide.—Bromination of sorbic acid yielded a crude dibromide which consisted of a solid, m. p. 94—95°, and a yellow liquid (compare Kachel and Fittig, *Annalen*, 1873, **168**, 287; Auwers and Heyna, *loc. cit.*). From the liquid, however, further

large quantities of the solid dibromide separated, and it is probable that the very small liquid residue consisted almost entirely of the solid form, since it did not yield a distinctive bromosorbic acid on treatment with diethylamine. Esterification of the solid dibromide yielded the *methyl* ester, a pleasant-smelling liquid, b. p. 146°/12 mm. (Found : Br, 56·0. $C_7H_{10}O_2Br_2$ requires Br, 55·9%). The same compound was obtained by addition of bromine to pure methyl sorbate.

Bromosorbic acid was obtained by treating an ethereal solution of solid sorbic acid dibromide with diethylamine. It crystallised from benzene–petroleum in white plates, m. p. 140° (Found : Br, 41·8. $C_6H_7O_2Br$ requires Br, 41·9%). The *methyl* ester of this acid was obtained in similar fashion from the methyl ester of solid sorbic acid dibromide (above). It was a pleasant-smelling, yellow oil, b. p. 104—106°/10 mm. (Found : Br, 38·8. $C_7H_9O_2Br$ requires Br, 39·0%).

Removal of hydrogen bromide from the small liquid residue obtained in the bromination of sorbic acid yielded a bromosorbic acid, m. p. 140°, identical with that described above.

Reduction of Bromosorbic Acid.—When this acid was reduced in the usual way with zinc dust and acetic acid, a halogen-free, brown oil was obtained which soon solidified. After recrystallisation, it melted at 140° and was identical with ordinary sorbic acid. To avoid geometrical inversion which had possibly occurred, milder reducing agents were tried, but reduction could not be effected therewith.

B. Addition of Esters.

Methyl β-methyl-Δ^{γ}-pentene-$\alpha\alpha\varepsilon$-tricarboxylate was obtained, in 60—70% yield, by addition of methyl malonate to methyl sorbate under essentially the conditions described by Kohler and Butler (*loc. cit.*). The ester corresponded in boiling point with that obtained by Kohler and Butler.

Condensation was also attempted under other conditions. Employment of an ethereal, alcohol-free suspension of ethyl sodiomalonate with methyl sorbate at room temperature yielded a product containing methyl methylpentenetricarboxylate, products derived therefrom by internal condensation, and polymeric products from methyl sorbate. With diethylamine as condensing agent and methyl cyanoacetate as addendum, no addition occurred; there was a similar result when these substances were brought together under Guareschi's conditions. When alcoholic methyl sodiomalonate was employed, subsidiary condensations proceeded too far to allow isolation of any pure product.

Methyl Δ^{γ}-pentene-$\alpha\alpha\varepsilon$-tricarboxylate was obtained in a similar

way by adding methyl malonate to methyl β-vinylacrylate. This ester, prepared by esterification of the pure acid with methyl alcohol and sulphuric acid, could be stabilised for a considerable time by addition of a small quantity of quinol immediately after distillation. In most of the condensations no appreciable quantity of the latter ester was recovered unchanged. The addition product distilled at 178—180°/17 mm. (172°/13 mm. on redistillation. Kohler and Butler give a lower b. p., 147—151°/11 mm.). The *triamide* was formed in almost quantitative yield when the ester was allowed to stand with alcoholic ammonia. It formed colourless prisms, m. p. 213° (Found : C, 48·5; H, 6·7. $C_8H_{13}O_3N_3$ requires C, 48·2; H, 6·5%).

Methyl Ethyl β-Cyano-γ-methyl-Δ$^{\delta}$-hexene-βζ-dicarboxylate.—To a solution of sodium (2·3 g.) in the minimal quantity of absolute methyl alcohol, ethyl methylcyanoacetate (12·8 g.) and sufficient dry ether to produce a permanent turbidity were added. Methyl sorbate (12·6 g.) was then dissolved in the solution, and the whole refluxed on a steam-bath for 6 hours. More ether was added to the cooled product, which was then poured into water and worked up in the usual way. The oil so obtained yielded unchanged esters and a product (2 g.) of b. p. 185—188°/16 mm. In each of three such additions, a similar yield was obtained. When, however, only one-eighth of the sodium theoretically required was used and the refluxing continued for 5 hours, the yield of addition product rose to 60—70%. The latter was a pale yellow, mobile oil (Found : C, 61·8; H, 7·4. $C_{13}H_{19}O_4N$ requires C, 61·6; H, 7·5%).

Methyl ethyl β-cyano-Δ$^{\delta}$-hexene-βζ-dicarboxylate was prepared in similar fashion to the preceding ester, ethyl methylcyanoacetate (2 mols.), methyl β-vinylacrylate (1 mol.), and sodium (1/8 atom) being used. Refluxing for more than 5 hours resulted in a diminished yield. The ester was a pale yellow, mobile oil, b. p. 182—185°/16 mm. (Found : C, 60·3; H, 7·0. $C_{12}H_{17}O_4N$ requires C, 60·25; H, 7·1%).

Attempted Addition of Esters to Methyl Δ$^{\gamma}$-Pentene-ααε-tricarboxylate.—In order to ascertain the mobility or fixity of the double bond in methyl pentenetricarboxylate, attempts were made to secure addition of methyl cyanoacetate, (1) using sodium as condensing agent under the conditions described above, and (2) under Guareschi's conditions. In neither case did addition take place.

Attempted Addition of Methyl Malonate and Methyl Cyanoacetate to Methyl Crotonylidenemalonate.—Methyl crotonylidenemalonate was synthesised by the method of Meerwein (*Annalen*, 1908, **358**, 82). All attempts by the above-described methods to secure its

condensation with methyl malonate failed. Condensation with methyl cyanoacetate under Guareschi's conditions also did not succeed. Attempts to prepare by Meerwein's method the probably more reactive methyl crotonylidenecyanoacetate were unsuccessful.

C. Oxidations.

Ozonisation of Vinylacrylic Acid Dibromide.—Through a solution of the solid dibromide (10 g.) (p. 1062) in 60 c.c. of chloroform, mixed with 10 c.c. of water, a rapid stream of ozonised oxygen was passed for 6 hours. The issuing gases were led through aqueous ammonia to absorb any formaldehyde carried from the decomposition vessel.

The absence of formaldehyde was demonstrated by the hexamethylenetetramine test. The aqueous and the chloroformic layer were separated. A portion of the former, acidified with acetic acid, yielded with calcium chloride a thick precipitate of calcium oxalate; from the remainder a quantity of pure oxalic acid was isolated. The chloroformic layer was evaporated at room temperature. The residue, a pale yellow oil, was warmed for ½ hour with aqueous potassium acetate (8 g. in 12 c.c. of water). The deep yellow, lachrymatory *α-bromoacraldehyde* so produced was distilled in steam and extracted with ether; it was obtained, after removal of the solvent and distillation, as a pale yellow oil, b. p. 58°/21 mm. (Found: Br, 59·2. C_3H_3OBr requires Br, 59·25%). It yielded a *semicarbazone*, m. p. 160°, which was identical with that obtained from a specimen of α-bromoacraldehyde synthesised by the method of Auwers and Heyna (*loc. cit.*).

The liquid dibromide also was oxidised in a similar way and yielded the same degradation products. No compounds arising from αβ- or αδ-dibromides could be found among the oxidation products.

Ozonisation of Methyl Methylpentenetricarboxylate (I) *and Methyl Pentenetricarboxylate* (II).—The oxidation of these substances was conducted in a similar way to that described by Kohler and Butler (*loc. cit.*) and yielded precisely similar results.

Ozonisation of Methyl Ethyl Cyanomethylhexenedicarboxylate (III).—The ester (10 g.), dissolved in dry chloroform (30 c.c.), was submitted to a current of ozonised oxygen for 36 hours. On evaporation of the chloroform under diminished pressure, the ozonide was obtained as a viscous, faintly yellow oil. This was decomposed by heating with water (30 c.c.) for 2 hours, the escaping vapours being passed into a solution of *p*-nitrophenylhydrazine hydrochloride. The yellow precipitate (m. p. 126° after recrystallisation) which formed in the latter was identified as acetaldehyde-*p*-nitrophenylhydrazone by comparison with an authentic specimen.

The aqueous liquor was mixed with 30% hydrogen peroxide

(50 c.c.). After 12 hours, the aqueous portion was decanted, and the oil hydrolysed by boiling with 40% potassium hydroxide solution (30 c.c.) until no more ammonia was evolved (5 hours). The cooled alkaline liquid yielded, on acidification and extraction, a gummy acid which partly crystallised. This was esterified with alcohol and sulphuric acid and distilled. The colourless ester, b. p. 125—132°/12 mm., was re-hydrolysed with alcoholic potassium hydroxide; a solid potassium salt separated which yielded an acid, m. p. 123°, and the alcoholic liquor yielded a second acid, m. p. 195°. These acids were identified by their basicity and by comparison with authentic specimens as *cis*- and *trans*-forms, respectively, of *s*-dimethylsuccinic acid.

Ozonisation of Methyl Ethyl Cyanohexenedicarboxylate (IV).—The method was that employed in the preceding oxidation. The only substances that could be isolated were acetaldehyde (identified as the *p*-nitrophenylhydrazone, m. p. 126°) and a cyano-ester which yielded a considerable quantity of methylsuccinic acid, m. p. 112° (identified by basicity and comparison with an authentic specimen).

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LONDON, S.W. 7. [*Received, January* 31*st*, 1927.]

CXLIV.—*The Alkaloids of Ipecacuanha. Part IV.*

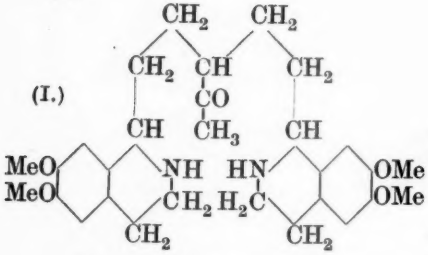
By WILLIAM HARRISON BRINDLEY and FRANK LEE PYMAN.

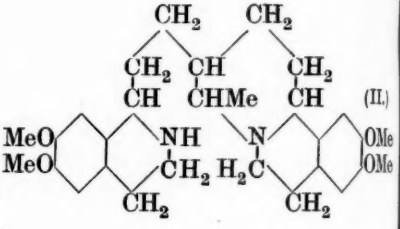
IN the earlier parts of this series (Carr and Pyman, J., 1914, **105**, 1591; Pyman, Part II, J., 1917, **111**, 419; Pyman, Part III, J., 1918, **113**, 222), the formula $C_{29}H_{40}O_4N_2$ was established for emetine, and Hesse's observation (*Pharm. J.*, 1898, **7**, 98) that it contains four methoxyl groups, and Keller's discovery (*Arch. Pharm.*, 1911, **249**, 512) that it is a secondary-tertiary base, were confirmed. The relations of emetine to its subsidiary alkaloids were determined, and many reactions of these bases were described. It was shown that emetine is a derivative of *iso*quinoline, since it gave 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid on oxidation.

Some two years ago, Professor Robert Robinson, F.R.S., suggested, on the basis of a theory of structural or genetic relationships of alkaloids of the *iso*quinoline group, that emetine and its congeners might be derived from two molecules of dihydroxyphenylalanine, two molecules of glyceraldehyde, and one molecule of dihydroxy-

acetone by processes of condensation, decarboxylation, methylation, and reduction. Coming closer to normal laboratory syntheses in order to simplify the discussion, one might imagine the condensation of two molecules of acraldehyde and one molecule of acetone to the ketone-dialdehyde,* $(CHO{\cdot}CH_2{\cdot}CH_2)_2CH{\cdot}CO{\cdot}CH_3$, and the subsequent condensation of this intermediate with β-(3 : 4-dimethoxyphenyl)ethylamine to the *iso*quinoline derivative (I).

(I.)





(II.)

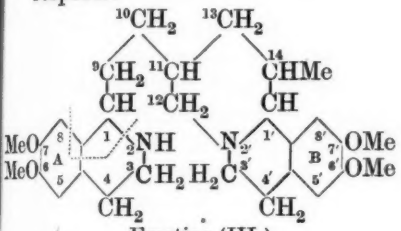
On reduction and dehydration, (II) is obtained, and this, it was thought, might be the constitution of emetine. Recently, this field of work has been entered by Späth and Leithe (*Ber.*, 1927, **60**, 688), who have put forward a partial formula for emetine in harmony with the above formula (II), in that it contains two dimethoxy-*iso*quinoline residues connected through the 1-position in each case. It has consequently become necessary to publish Robinson's formula at once. Whilst this formula is able to afford an explanation of most of the salient facts in the chemistry of the alkaloids related to emetine, there is undoubtedly a difficulty in connexion with the nature of rubremetine.

Oxidation of emetine with ferric chloride, bromine, or iodine, or of *O*-methylpsychotrine with bromine or iodine, yields the deep red rubremetine salts, *e.g.*, rubremetinium chloride, $C_{29}H_{33}O_4N_2Cl$, in which one of the nitrogen atoms has lost its basicity and the other has become quaternary (Carr and Pyman; Pyman, Part II, *loc. cit.*; Karrer, *Ber.*, 1916, **49**, 2057).

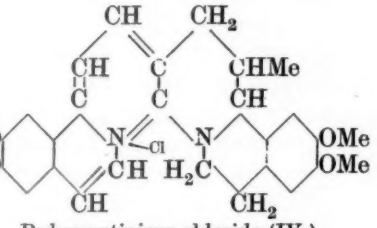
It would appear, therefore, that the removal of eight hydrogen atoms from emetine in the process of oxidation to rubremetine should be accompanied by some structural change which could destroy the salt-forming power of one of the nitrogen atoms. This would hardly be the case with rubremetine formulæ derived from (II) by simple oxidation of two of the three hydrogenated pyridine rings, and in this respect Robinson's formula for emetine seems to us unsatisfactory. It has led us, however, to put forward a formula

* The type $R_2CH{\cdot}CO{\cdot}CH_3$ was preferred to $R{\cdot}CH_2{\cdot}CO{\cdot}CH_2R$ because cuskhygrine is a representative of the former class.

for emetine (III), differing from Robinson's only in the position of the *C*-methyl group, which affords a convincing explanation of the formation of rubremetine (IV), and is equally satisfactory in other respects.



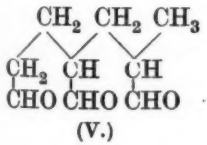
Emetine (III.)



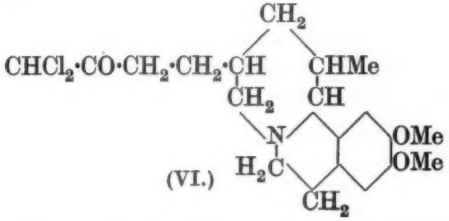
Rubremetinium chloride (IV.)

The loss of basicity of one of the nitrogen atoms in the conversion of emetine into rubremetine is thus attributed to amidine formation, a double bond connecting N(2) with C(12). Evidence is given below that *O*-methylpsychotrine, and therefore probably rubremetine also, contains a double bond between C(1) and C(9), and this necessitates a third double bond between C(10) and C(11) to complete the unsaturation of the new ring. The fourth double bond is assumed to lie between C(3) and C(4), thus giving the berberine-like structure for rubremetine shown above. This formula accords with the facts that rubremetine cannot be converted into derivatives analogous to oxyberberine or berberine-acetone. It is also in harmony with the fact that no substance analogous to rubremetine can be made by the oxidation of *N*-methylemetine with bromine.

Turning to the new formula for emetine (III) itself, it may be pointed out that the skeleton of this formula might be produced phytochemically by the condensation of two molecules of dihydroxyphenylalanine with a condensation product (V) derived from three molecules of glyceraldehyde.



(V.)



(VI.)

This process leads to two alternative formulæ for emetine, namely, (III), and a second formula in which the *C*-methyl group is attached to C(9) instead of C(14), but formula (III) is preferred for reasons given later. It may be pointed out, however, that in both formulæ this methyl group is shown in a position relative to an *iso*quinoline

ring, which it is known to occupy in other alkaloids, for example, corydaline.

The new formula for emetine permits the deduction of intelligible formulæ for the subsidiary alkaloids of ipecacuanha.

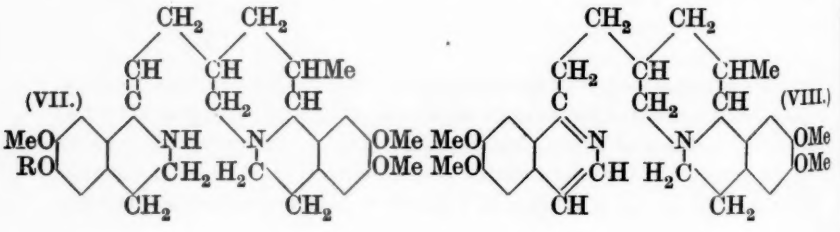
Cephæline, $C_{28}H_{38}O_4N_2$, contains a phenolic hydroxyl group in the place of one of the methoxy-groups of emetine, and yields emetine on methylation. It yields on oxidation with ferric chloride a base, $C_{20}H_{27}O_3NCl_2$, from which no nitrosoamine could be prepared, containing two methoxy-groups, and two chlorine atoms which were readily replaceable by hydroxyl (Carr and Pyman, *loc. cit.*), giving a compound $C_{20}H_{29}O_5N$, which appeared to have amphoteric character. The base $C_{20}H_{27}O_3NCl_2$ contains only one benzene nucleus (Dobbie and Fox, J., 1914, **105**, 1639), whence it follows that the benzene nucleus containing the phenolic hydroxyl group has been eliminated, together with one of the nitrogen atoms. The only explanation of the formation of the base $C_{20}H_{27}O_3NCl_2$ which seems to us plausible is indicated by dotted lines in the emetine formula (III), and leads to the conclusion that the phenolic hydroxyl group of cephæline must be placed in ring A, probably in position 6 of the *iso*quinoline ring. The choice of position 6 for this hydroxyl group is confirmed by evidence discussed below in connexion with psychotrine.

The properties of the base $C_{20}H_{27}O_3NCl_2$ are expressed by the formula (VI). Its conversion into the substance $C_{20}H_{29}O_5N$ by means of cold aqueous sodium hydroxide may be attributed to the formation of a substituted glyoxal, which then undergoes a change resembling the transformation of methylglyoxal into lactic acid. The substance $C_{20}H_{29}O_5N$ thus has the formula (VI) with

$$\cdot CH(OH)\cdot CO_2H$$

in place of $\cdot CO\cdot CHCl_2$.

Psychotrine, $C_{28}H_{36}O_4N_2$ (VII, R = H), yields on reduction cephæline and a stereoisomeride *iso*cephæline. *O*-Methylpsychotrine, $C_{29}H_{38}O_4N_2$ (VII, R = Me), yields on reduction emetine and *iso*emetine. They, therefore, contain a double linking, and saturation of this renders (at least) one additional carbon atom asymmetric (Carr and Pyman; Pyman, Parts II and III, *locc. cit.*) :



This condition can be fulfilled in many ways, but it is shown below that *O*-methylpsychotrine gives a good yield of psychotrine on partial hydrolysis with one molecule of acid. One of the four methoxy-groups is thus preferentially hydrolysed, and it must be in ring A, since cephæline, and therefore psychotrine, contains hydroxyl in this ring. It is suggested that the cause of the preferential hydrolysis is the presence of a double bond between C(1) and C(9), and that the methoxy-group in the para-position to the substituted vinyl group has become hydrolysed.

Confirmation of the situation of the double linking in the $\alpha\beta$-position to a benzene nucleus is afforded by the fact that *O*-methylpsychotrine yields on reduction, besides emetine and *iso*emetine, a demethoxyemetine or demethoxy*iso*emetine (base C, Part II, *loc. cit.*) in which one of the methoxy-groups has been replaced by hydrogen, for there is evidence (Semmler, *Ber.*, 1908, **41**, 2556; Salway, J., 1910, **97**, 2413) that a substituted vinyl group facilitates the replacement by hydrogen of alkyloxy-groups situated in the para-position with respect to it. The deep yellow colour of psychotrine base is also in accord with formula (VII).

The reason why formula (III) for emetine is preferred to that in which the *C*-methyl group is attached to C(9) is that *O*-methylpsychotrine gives emetine and *iso*emetine in fair yield on reduction, in spite of the complications introduced by demethoxylation, and it is therefore considered probable that only one additional carbon atom is rendered asymmetric by the reduction, giving two isomerides, whereas the alternative formula requires the rendering of two additional carbon atoms asymmetric, thus giving four possible isomerides.

Emetamine, $C_{29}H_{36}O_4N_2$ (VIII), is a ditertiary base yielding on reduction a mixture from which a small quantity of *iso*emetine can be isolated as benzoyl derivative. Emetamine is more feebly basic than *O*-methylpsychotrine (Pyman, Part II, *loc. cit.*), and may be regarded as containing the *iso*quinoline ring A in the unsaturated condition. Formula (VIII) accords with the facts that (1) although emetamine contains two atoms of hydrogen fewer than *O*-methylpsychotrine, it is not formed in the incomplete oxidation of *O*-methylpsychotrine to rubremetine, and (2) it cannot be converted into rubremetine.

The purity of the preparation of emetamine described in Part II has now been confirmed by the fractionation of a considerable quantity of this base, which has been characterised further by the preparation of a number of salts.

EXPERIMENTAL.

O-*Methylpsychotrine* has now been crystallised. It separates from hot dry ether in well-formed prisms, m. p. 123—124° (corr.) (Found: C, 73·0; H, 8·3. $C_{29}H_{38}O_4N_2$ requires C, 72·7; H, 7·9%). It is sparingly soluble in hot dry ether, almost insoluble in cold dry ether, but readily soluble in cold alcohol. In commercial absolute alcohol it had $[\alpha]_D$ + 43·2° (c = 1); $[\alpha]_D$ + 43·4° (c = 2·1); $[\alpha]_D$ + 43·2° (c = 3·9).

O-*Methylpsychotrine picrate* crystallises from acetone in octagonal plates which, after being dried at 100°, soften from 142° and gradually melt up to 175° (corr.).

Oxidation of O-*Methylpsychotrine.*—(1) *By permanganate.* The base from 6 g. of methylpsychotrine hydrogen oxalate in acetone (150 c.c.) was oxidised by the addition of a saturated aqueous solution of potassium permanganate (35 g.) in the course of ½ hour with thorough stirring, the temperature of the solution rising from 16° to 24°. After the products had been worked up as described in the oxidation of emetine by permanganate (Carr and Pyman, *loc. cit.*, p. 1630), the only crystalline product obtained was 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid (yield 0·16 g.), which was recognised by its appearance, content of water of crystallisation (Found: loss at 100°, 13·9. Calc., 13·4%), and behaviour on heating, the dried substance melting from 204° to 209° (corr.) according to the rate of heating, effervescing, and leaving an alkaline residue.

(2) *By chromic acid.* On adding aqueous chromic acid in excess to a warm aqueous solution of *O*-methylpsychotrine sulphate, a brown, gummy precipitate was obtained which became a bright yellow, crystalline powder on rubbing (Found, in substance dried at 100°: Cr, 13·9. $C_{29}H_{38}O_4N_2,H_2Cr_2O_7$ requires Cr, 14·9%). It was almost insoluble in water. This salt (1·6 g.) was suspended in water at 100° for 60 hours, the volume being kept at 60—70 c.c. The product was mixed with sodium hydroxide, extracted with ether (E), and filtered. The filtrate was acidified with hydrochloric acid, and extracted with chloroform, which left 0·25 g. of residue on distillation. A hot aqueous extract of this residue deposited rubremetine hydrochloride, recognised by its characteristic appearance and m. p. (air-dried, 125°; dried at 100°, from 160°). The ethereal extract (E) gave crude *O*-methylpsychotrine (0·45 g.), yielding 0·35 g. of the crystalline hydrogen oxalate from which the pure base (m. p. 123—124°) was readily obtained.

Partial Demethylation of O-*Methylpsychotrine.*—Methylpsychotrine sulphate heptahydrate (10 g.) and hydrochloric acid (1·54 c.c.; 34%) were heated for 6 hours at 170°. The product was dissolved

in water (50 c.c.) and shaken with ether, and excess of ammonia was added gradually; psychotrine (3·0 g.) then crystallised. This was dissolved in alcohol and mixed with an alcoholic solution of oxalic acid (1·5 g.); psychotrine hydrogen oxalate (3·2 g.) then separated (mother-liquor M). The filtrate from the psychotrine was separated into ethereal and aqueous layers and the former was extracted with aqueous sodium hydroxide (ethereal solution E). This was mixed with excess of ammonium chloride, combined with the aqueous layer and extracted with chloroform; the extract then gave with alcoholic oxalic acid more psychotrine hydrogen oxalate (2·1 g.). The mother-liquor from this and the mother-liquor M gave, after further similar treatment, another small crop (0·25 g.) of the same salt. The residue from the ethereal solution E gave, with alcoholic oxalic acid, methylpsychotrine hydrogen oxalate (2·4 g.).

The yields in this experiment and others in which the period and temperature of heating were varied appear below:

Time (hrs.).	Temp.	% Yield of psychotrine.	% Methylpsychotrine recovered.
3	150°	8	74
6	150	12	71
3	170	37	50
6	170	54	23

The psychotrine obtained by demethylation of methylpsychotrine was identical with the natural alkaloid. The bases from each source and mixtures of the two sintered from 115° and melted and effervesced at 122° (corr.), when air-dried, and softened from 122° and melted and effervesced at about 129° (corr.), after drying in a vacuum over sulphuric acid. Psychotrine from its methyl ether, like the natural base, crystallised from aqueous acetone in well-formed, yellow prisms containing $4H_2O$ (Found: H_2O, 13·3. Calc.: H_2O, 13·4%). Crystals from each source were found to be identical crystallographically by Mr. G. Greenwood, M.Sc., of the University of Manchester, to whom the authors are much indebted for his examination and for the following data:

Crystal system: orthorhombic. $a : b : c = 0{\cdot}989 : 1 : 1{\cdot}209$.
Forms observed: {100} {010} {110} + {101}.

Angle measured.	Natural psychotrine (obs.).	Psychotrine from its methyl ether (obs.).	Calc.
(100) : (101)	39° 20′	39° 18′	—
(110) : (101)	56° 35′	56° 41′	—
(100) : (110)	44° 38′	44° 50′	44° 41′

Mr. Greenwood adds: "It is interesting that the ratio $a : b$ is so near to 1 : 1 and the angle (100) : (110) to 45°. If this were actually the case, the crystal would be tetragonal. I am afraid the

angle measurements were really not good enough to settle this point. Also the crystals were too poor to examine the optical properties, which would again have decided this question. However, judging from the geometrical properties of the faces on the ends of the crystals, I think that there is no doubt that the crystals are not tetragonal and that the equality of *a* and *b* is merely a chance effect."

Psychotrine hydrogen oxalate readily separates in nearly colourless needles when alcoholic solutions of its constituents are mixed. It is very sparingly soluble in alcohol, but readily soluble in water. After drying in a vacuum over sulphuric acid, it softens from 130° and melts and effervesces up to 145° (corr.) [Found, (*a*) in salt crystallised from water, (*b*) in salt from alcohol: loss in vacuum over H_2SO_4, (*a*) 10·3; (*b*) 9·0. $C_{28}H_{36}O_4N_2,2C_2H_2O_4,4\frac{1}{2}H_2O$ requires loss of $4H_2O$, 10·0%. Found in dried salt: C, 58·7, 58·6; H, 6·6, 6·6. $C_{28}H_{36}O_4N_2,2C_2H_2O_4,\frac{1}{2}H_2O$ requires C, 58·8; H, 6·3%].

Emetamine.

Purification of Emetamine.—111 G. of emetamine hydrogen oxalate having $[\alpha]_D - 5°$, prepared by the method described earlier (Pyman, Part II, *loc. cit.*), were subjected to further fractionation as follows. The base was regenerated in chloroform by means of sodium hydroxide, and extracted six times with sufficient 2% sulphuric acid to remove 5% of the base at each extraction. Each extract and the mother-liquor were then basified, and the extracted bases were converted separately into the hydrogen oxalates. The yields and specific rotatory powers (of air-dried salt in water; $c = 4$) were as follows: (1) 4·6 g. (coloured); (2) 5·2 g., $[\alpha]_D - 4·7°$; (3) 5·0 g., $[\alpha]_D - 5·7°$; (4) 4·6 g., $[\alpha]_D - 6·2°$; (5) 5·0 g., $[\alpha]_D - 6·0°$; (6) 5·2 g., $[\alpha]_D - 6·4°$; remainder 55·7 g., $[\alpha]_D - 6·3°$. The last fraction, which was regarded as pure, was converted into the base, and through this into other salts. Its specific rotatory power is in close agreement with that previously recorded ($[\alpha]_D - 6·0°$).

Emetamine.—When emetamine is regenerated, in chloroform, from a salt and crystallised from ethyl acetate, it is free from solvent and melts at 153—154° (corr.) [Pyman, *loc. cit.*, gives 155—156° (corr.)], but when it is regenerated in ether, the ethereal solution, after being dried for a few minutes over potassium carbonate and filtered, deposits emetamine in colourless needles containing solvent of crystallisation. In this form, the air-dried base has m. p. 138—139° (corr.), and $[\alpha]_D + 13·6°$ in commercial absolute alcohol ($c = 2·2$); after drying in a vacuum at 100°, the base has m. p. 142—143° (corr.). It appears to contain $\frac{1}{2}$ mol. of ether of crystallisation [Found, in air-dried base: loss at 100° in a vacuum, 7·1; loss over

H_2SO_4, 6·9; C, 71·6, 71·6, 71·7; H, 7·3, 7·4, 7·9. $C_{29}H_{36}O_4N_2,\frac{1}{2}Et_2O$ requires loss of $\frac{1}{2}Et_2O$, 7·2; C, 72·4; H, 8·0%. Found, in dried base: *M* (in camphor), 447. $C_{29}H_{36}O_4N_2$ requires *M*, 476]. Emetamine of m. p. 153—154° can be converted into the lower-melting form by preparing a salt and regenerating the base in ether, but not by simple crystallisation from ether. On the other hand, emetamine of m. p. 138—139° yields the base of m. p. 153—154° on drying and crystallisation from ethyl acetate after seeding with the variety of higher m. p.

Emetamine hydrogen oxalate prepared from the pure base contained $3H_2O$, had $[\alpha]_D$ — 6·1° in aqueous solution ($c = 4·4$), and effervesced at 172° (corr.), these figures being in close agreement with those previously found for this salt (Pyman, *loc. cit.*).

Emetamine hydrochloride crystallises from concentrated hydrochloric acid in colourless, glistening needles; these, if air-dried, melt at 77—80°, but after being dried in a vacuum over sulphuric acid, the salt softens and effervesces at 218—223° (corr.) (Found, in air-dried salt: loss in a vacuum over H_2SO_4, 21·9; loss at 100°, 21·9. $C_{29}H_{36}O_4N_2,2HCl,8\frac{1}{2}H_2O$ requires H_2O, 21·8%. Found, in dried salt: Cl, 12·5. $C_{29}H_{36}O_4N_2,2HCl$ requires Cl, 12·9%). The hydrated salt had $[\alpha]_D$ — 17·5° in aqueous solution ($c = 4·1$). It is very readily soluble in cold water.

Emetamine hydriodide is deposited as an oil on adding sodium iodide to an aqueous solution of the hydrochloride. A solution of the oil in methyl alcohol, on spontaneous evaporation, deposits the salt in a microcrystalline form which (dried at 100°) softens from 208° and effervesces up to 274°.

Emetamine nitrate is precipitated in rosettes of acicular prisms on the addition of dilute nitric acid to an aqueous solution of the hydrochloride. After crystallisation from water, it forms prismatic needles.

The air-dried salt has m. p. 165—166° (corr.), and $[\alpha]_D$ — 7·3° in aqueous solution ($c = 2·6$) (Found, in air-dried salt: loss in a vacuum over H_2SO_4, 5·8. $C_{29}H_{36}O_4N_2,2HNO_3,2H_2O$ requires H_2O, 5·6%. Found, in dried salt: C, 58·0; H, 6·3. $C_{29}H_{36}O_4N_2,2HNO_3$ requires C, 57·8; H, 6·3%). On heating this salt at 100° either in the dry state or in strong aqueous solution, decomposition takes place.

Emetamine picrate is precipitated on mixing hot alcoholic solutions of the base (1 mol.) and picric acid (2 mols.), and after crystallisation from acetone forms long, yellow needles, which, after drying at 100°, begin to soften at 147° and gradually melt and effervesce up to 173° (corr.). It is very sparingly soluble in hot water, hot alcohol, or cold acetone.

Attempts to prepare emetamine acetate, salicylate, sulphate, and tartrate in crystalline form were unsuccessful.

Emetamine dimethiodide was prepared by heating the base with methyl iodide for 7 hours at 100°. It crystallised from aqueous alcohol in prismatic needles, which began to effervesce at 238° (corr.) (Found, in air-dried salt: loss at 110°, 2·2. $C_{31}H_{42}O_4N_2I_2,H_2O$ requires H_2O, 2·3%. Found, in dried salt: I, 33·0. $C_{31}H_{42}O_4N_2I_2$ requires I, 33·4%).

Action of Bromine upon Emetamine.—The base from emetamine hydrogen oxalate (1·8 g.) in chloroform (30 c.c.) was mixed with bromine (0·25 c.c.) in chloroform (10 c.c.). After 5 minutes, the solution was shaken with ammonia and dried with potassium carbonate, and the solvent was removed. The residue was extracted with boiling water, and the extract concentrated; it then deposited less than 0·1 g. of a red, microcrystalline substance, resembling rubremetine hydrobromide in colour and sparing solubility in water, but melting, when air-dried, at 185—190°. (Air-dried rubremetine hydrobromide melts at about 115—120°.) The material insoluble in hot water was dissolved in dilute hydrochloric acid, and the bases were liberated by ammonia in the presence of ether, a considerable amount of dark brown resinous material being precipitated; the ethereal solution gave a residue (0·3 g.), from which emetamine hydrogen oxalate (0·25 g.; m. p. 165—170°) was prepared.

Reduction of Emetamine.—(a) *With sodium and alcohol.* In view of the importance attaching to the formation of benzoyl*iso*emetine from emetamine (Part II, p. 443), the reduction of emetamine with sodium and alcohol was repeated, the specially purified emetamine described above being used, and the formation of *iso*emetine was confirmed by the isolation of its benzoyl derivative.

(b) *With tin and hydrochloric acid.* The reduction of emetamine by this means proceeds very slowly, and in the following experiment much emetamine was recovered unchanged, but again benzoyl-*iso*emetine was readily obtained from the reduced portion.

The base regenerated from emetamine hydrogen oxalate (3·55 g.) was heated with alcohol (20 c.c.), concentrated hydrochloric acid (20 c.c.), and tinfoil (8 g.) for 13 hours under reflux. The base (1·3 g.), regenerated in ether, was converted into hydrogen oxalate in alcohol; crude emetamine hydrogen oxalate (1·1 g.) then crystallised. The base (0·4 g.) regenerated from the mother-liquor was mixed with benzoic anhydride (0·4 g.) in dry ether; the deposited benzoyl*iso*emetine (0·08 g.), after being washed with acetone, melted at 207° (corr.), alone or mixed with a known specimen of benzoyl*iso*emetine.

The authors desire to thank Professor Robert Robinson, F.R.S., for the very considerable help which he has given them by suggestion and discussion in determining the constitution of the alkaloids of ipecacuanha, and to thank Mr. J. A. Goodson, F.I.C., for assistance in the earlier stages of the separation of emetamine from *O*-methylpsychotrine.

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CXLV.—*The Periodic Electro-deposition of Metals through Secondary Reaction.*

By ERNEST SYDNEY HEDGES.

EXPERIMENTS described in a series of papers by the present author (J., 1926, 1533, 2580, 2878) have shown that periodic changes in current density and potential occur in the electrolytic dissolution of a number of metals in various electrolytes. The present communication contains an account of the inversion of this process—the periodic deposition of a metal at the cathode.

The method of investigation was essentially similar to that in the experiments on the anode (*loc. cit.*) but certain important improvements were made: Instead of measuring the total *P.D.* across the electrolytic cell, the *P.D.* between the cathode alone and a standard reference electrode was determined. Also, the measurements were made by a static instrument, so that absolutely no current was taken from the system. Since it was anticipated that rapid alterations of potential would have to be followed, a string electrometer was used as the measuring instrument. This has the advantage that it is entirely dead-beat, and can therefore be used for following very rapid vibrations, and its sensitivity is adjustable over a wide range.

The same electrolysis vessel was used as before, but it was now provided with a side-tube leading to a bridge of *N*-potassium chloride, making connexion with a *N*-potassium chloride calomel half-element. The cathode was connected to the string of the electrometer and the calomel cell was earthed. During electrolysis, the *C.D.* was progressively raised and the position of the fibre was noted on the scale in the eye-piece, the scale being adjusted so that 25 divisions corresponded to 1 volt. All the experiments were conducted at 30° and a platinum anode was used throughout.

Periods in Direct Deposition.

The conditions of the first experiments were designed to be as nearly as possible analogous to those known to be favourable to periodicity at the anode. Thus, attempts were directed towards depositing a metal in presence of an acid which would dissolve it, in the anticipation of reaching a boundary state where a deposit of metal would form and dissolve off alternately. Experiments of this type on the deposition of iron and of zinc from various solutions of their salts in presence of acids met with no result.

It was hoped to realise a periodic deposition of alkali metals in the electrolysis of solutions of their salts with a mercury cathode, for here there is a possibility of a balance between the rate of deposition of the metal and the rate of dissolution by the water. Experiments with $2N$-, N-, and $N/10$-solutions of alkali salts were unsuccessful. However, it seems that at these concentrations the sodium dissolves off the cathode too easily, for later experiments have shown that periods can be realised in the electrolysis of $4N$-caustic soda with a mercury cathode.

Actually, periods were observed by Coehn (*Z. Elektrochem.*, 1901, **7**, 633) in the electrolysis of caustic soda with a mercury cathode, although experimental details are not given. The experiment was repeated by Kremann and Lorbeer (*Sitzungsber. Akad. Wiss. Wien*, April, 1913) using $3N$-caustic soda. The present author has confirmed these results and finds that the phenomenon is readily reproduced at 30° with $4N$-caustic soda, at a *C.D.* of 300 milliamp./cm.^{2}. Alternate periods of amalgam formation and dissolution took place, the periods becoming longer with time. The electrical change was very slight, the cathode *P.D.* being $-$ 2·08 volts during amalgam formation and $-$ 2·00 volts during dissolution of the amalgam.

There seems little doubt that the periods mentioned by Förster (*Z. Elektrochem.*, 1902, **8**, 500) in the deposition of copper from a nitric acid solution of the nitrate, and by Coehn (*ibid.*, p. 499) in electrolysing a solution of nitric acid in which bismuth had been dissolved, were due to a similar cause. The phenomenon mentioned by the present author (J., 1926, 1543) concerning a copper anode in nitric acid was probably due to periodicity at the cathode, where deposition of copper took place.

During the experiments on film formation at an unattackable anode (J., 1926, 2591), it was sought to deposit mercuric cyanide and cadmium cyanide, respectively, at the anode by electrolysing solutions of potassium mercuric cyanide or potassium cadmium cyanide; although this deposition did not occur, yet in both cases, between certain current densities, a periodically fluctuating potential

appeared, which had its source in the *cathode*, at which a periodic evolution of hydrogen bubbles was visible. The interpretation then placed on the phenomenon was that at the cathode, which had now become mercury (or cadmium) by deposition, potassium ions were discharged and periodically reacted with the solution giving hydrogen. In fact, this led to the experiments described above with alkali-metal salts.

Since the experiments on the deposition of sodium and potassium at similar concentrations at a mercury cathode gave negative results, attention was directed to the simultaneous deposition of mercury and potassium at a platinum cathode.

Experiments on the Simultaneous Deposition of Metals.

Preliminary experiments showed that a $N/10$-solution of mercuric chloride was almost non-conducting, and the small amount of product formed at the cathode appeared to be calomel. This is not surprising since, according to Luther (*Z. physikal. Chem.*, 1901, 36, 402), a solution of mercuric chloride saturated at 25° contains $1{\cdot}5 \times 10^{-4}$ mol. per litre of the $HgCl^{\cdot}$ ion and only 10^{-8} of the $Hg^{\cdot\cdot}$ ion. It was found, however, that deposits of mercury were readily formed when the solution also contained $N/10$-potassium chloride or $N/10$-hydrochloric acid. It may be noted that, since the solution contains practically no mercuric ions, the mercury is deposited through a secondary reaction, *i.e.*, either potassium or hydrogen is discharged first and reacts with the complex $HgCl_4''$ ion, and perhaps with undissociated $HgCl_2$.

The Deposition of Potassium with Mercury.—Periods were first observed in the electrolysis of a solution containing $N/10$-mercuric chloride and $N/10$-potassium chloride, using a *C.D.* of 16 milli-amp./cm.^{2}. The cathode potential then oscillated between $-1{\cdot}6$ and $-2{\cdot}0$ volts in periods of 1 minute. (Normal calomel electrode taken as zero.) In these experiments, two platinum electrodes, each of 12 sq. cm. available area, were used, although the cathode necessarily soon became a mercury electrode. Periods were obtained under similar conditions when an electrode of pure mercury was used, but it seemed better for practical reasons to use a cathode of platinum and allow the deposited metal to form a coating thereon.

It was evident that these periods required the simultaneous deposition of two metals, for when such a system was oscillating the electrodes were removed and placed in $N/10$-potassium chloride and $N/10$-mercuric chloride separately. No periods could be obtained in either solution, but when the electrodes were put back into the original solution of the mixed substances the periods continued.

At first, certain difficulties were encountered in the reproduction of these results, and these were traced to the fact that during electrolysis the ratio of mercury to potassium in the solution continuously diminishes; for ultimately the mercury is entirely deposited, whilst the potassium content of the solution remains unaltered. One source of difficulty was that at the commencement of the electrolysis, when the solution was rich in mercuric chloride, a film of mercurous chloride tended to form on the cathode. This could be loosened and thrown off the cathode by breaking and making the circuit several times in succession, or by increasing the cathode potential to the point of incipient hydrogen evolution.

A second inconsistency was that the conditions of formation of the periods appeared to differ in each experiment and did not correspond with any definite values of *C.D.* and potential. The general relations were these : below a certain critical *C.D.* mercury was deposited; above a higher critical *C.D.* hydrogen was evolved (potassium ions discharged); between these limits the electrode oscillated from one state to the other in regular periods. But the limits of the region of periodicity varied continuously throughout the course of the electrolysis. This was traced to the change in the concentration of the mercuric chloride, and it appeared that the critical limits of *C.D.* were lower the greater the ratio of potassium to mercury in the solution. Thus, a mixture consisting of $N/40$-mercuric chloride and $N/10$-potassium chloride gave a continuous evolution of hydrogen at the lowest *C.D.*'s, whilst a mixture consisting of $N/5$-mercuric chloride and $N/10$-potassium chloride required initially a high *C.D.* in order to reach the lower limit of the region of periodicity, although this critical *C.D.* fell continuously as the solution became weaker in mercuric chloride.

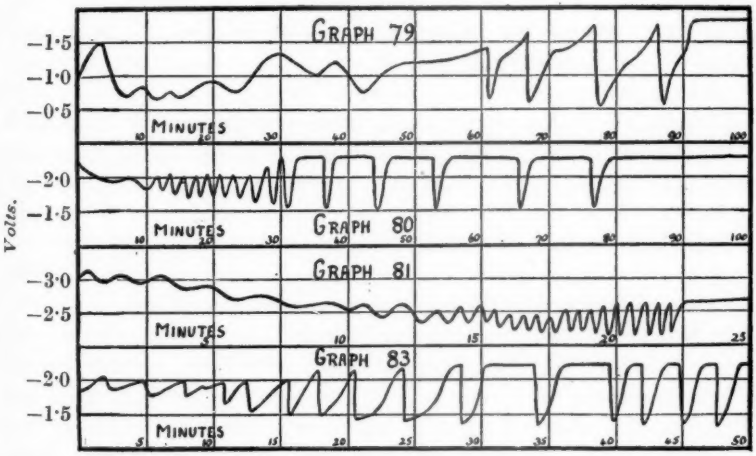
The use of a mercury anode would *increase* the concentration of mercury continuously, even if it were permissible in a chloride solution. The composition of the solution could be kept constant by employing a saturated solution of mercuric chloride in potassium chloride in presence of excess of solid mercuric chloride. Although this has not been done in the system under discussion, it has been done in other systems, and the resulting waves have been regular and continuous.

The most favourable mixtures were solutions containing $N/10$- or $N/20$-mercuric chloride and $N/10$-potassium chloride, and the method devised for securing comparable conditions was to electrolyse with a constant *C.D.* of 42 milliamp./cm.^{2}. This was below the critical *C.D.* required at the commencement of the electrolysis, but, owing to the gradual deposition of the mercury, after a time the solution reached a composition such that this *C.D.* produced

periods, and finally the *C.D.* employed corresponded to the upper limiting value for the solution, causing steady evolution of hydrogen.

Thus, for a given composition of solution there exists a current density-region of periodicity, and for a given *C.D.* there is a composition-region of periodicity. The latter is illustrated by Graphs 79 and 80, showing the transition of the electrode from the state of mercury deposition, through the region of periodicity, and into the state of continuous hydrogen evolution. Graph 79 represents the change with time of the cathode potential in the electrolysis of a mixture containing $N/20$-mercuric chloride and $N/10$-potassium chloride, using a *C.D.* of 9 milliamp./cm.^{2}. Graph 80 similarly represents the electrolysis of $N/10$-mercuric chloride and

FIG. 1.



$N/10$-potassium chloride with a *C.D.* of 42 milliamp./cm.^{2}. The periods have an amplitude of about 0·8 volt. At the more negative values of potential very strong evolution of hydrogen occurred in the form of small bubbles and the surface was dull through the formation of potassium amalgam, whilst at the less negative values the mercury was bright and only a few large bubbles of hydrogen adhered to it.

Deposition of other Metals with Mercury.—Similar periods were obtained in the simultaneous deposition of sodium and mercury. Graph 81 records the variation of the cathodic potential with time in the electrolysis of a solution containing $N/10$-mercuric chloride and $N/10$-sodium sulphate with a *C.D.* of 42 milliamp./cm.^{2}. During the first stage of the reaction, mercury was deposited and the electrode became covered with a few large bubbles of hydrogen. In the second, oscillatory stage, violent evolution of hydrogen in

the form of small bubbles occurred at regular intervals, whilst after 22 minutes steady hydrogen evolution set in. The initial fall of *P.D.* is due to the gradual increase in conductivity of the solution due to the liberated chlorine ions from the complex anions. The periods were fairly rapid, having an interval of 30 seconds.

Equally good periods were obtained in the electrolysis of a solution of *N*/10-mercurous nitrate and *N*/10-sodium nitrate.

A solution of *N*/10-mercuric chloride and *N*/10-barium chloride electrolysed with a *C.D.* of 4 milliamp./cm.^{2} gave excellent periods, the cathode *P.D.* changing from $-0{\cdot}8$ to $-1{\cdot}8$ volts every 30 seconds. Similarly, with a solution containing *N*/10-mercuric chloride and *N*/10-strontium chloride the *P.D.* oscillated between $-1{\cdot}7$ and $-2{\cdot}4$ volts in 2-minute periods, using a *C.D.* of 42 milliamp./cm.^{2}. Graph 83, which was obtained with *N*/10-mercuric chloride and *N*/10-calcium chloride under the same *C.D.*, is typical of the results obtained with these mixtures.

Periods were also obtained in the electrolysis of a solution of *N*/10-mercuric chloride and *N*/10-aluminium sulphate. These were somewhat irregular, but had an average interval of 2 minutes and an amplitude of about 0·4 volt.

Periods were not observed under any conditions in the electrolysis of solutions containing *N*/10-mercuric chloride with an *N*/10-solution of magnesium, zinc, copper, or nickel sulphate.

It was of interest to determine whether positive amalgam formation was necessary for the production of periods, or whether the direct discharge of hydrogen could produce a similar effect, and therefore the electrolysis of a solution containing *N*/10-mercuric chloride and *N*/10-hydrochloric acid was investigated. When hydrogen evolution started, however, the gas left the cathode in the form of very large bubbles, so that a constant *P.D.* could not be obtained and it was not possible to decide the point. Similar experiments at a cadmium cathode (*vide infra*), however, show that in this case hydrogen cannot act in such a way.

Deposition of Metals with Cadmium.—The salts of cadmium resemble those of mercury in their tendency to complex formation, and it is not surprising, therefore, to find a similar behaviour in the simultaneous deposition of cadmium and sodium. A solution containing *N*/5-cadmium nitrate and *N*/10-sodium sulphate gave at low *C.D.*'s a deposit of cadmium on the cathode, whilst at high *C.D.*'s a gelatinous film of cadmium hydroxide formed round the cathode and hydrogen was evolved. Intermediate *C.D.*'s covered a wide region in which the film of cadmium hydroxide formed periodically, whilst the cathode *P.D.* oscillated regularly between $-2{\cdot}25$

and — 2·4 volts; in these periods it was at the higher negative value while the film was on the electrode and hydrogen was being evolved, and at the lower potential the film as a whole slipped off the cathode, and metallic cadmium was deposited.

The following table shows that the frequency of these periods increases rapidly with increase of *C.D.* (The reverse was found to hold for the anodic periods, *q.v.*)

Milliamp./cm.^{2}	13	15	17	25	33	42	58
Period (secs.)	26	19	14	7	5	3	2

The only difference between these periods and those with mercury is that cadmium hydroxide is formed at the cathode in place of metallic mercury. This is due to the relative ease with which the oxide of mercury is reduced.

As it is not necessary further to multiply instances, experiments have not been conducted with other alkali metals and cadmium, although there is every reason to suppose that they would behave similarly. It was of interest, however, to examine the effect of hydrogen itself, and solutions containing *N*/5-cadmium nitrate and *N*/2-, *N*/5-, and *N*/10-sulphuric acid, respectively, were electrolysed. No periods were observed.

Deposition of other Metals with Alkali Metals.—Electrolysis of solutions of zinc sulphate with sodium sulphate gave no periods, and negative results were likewise obtained in electrolysing mixtures of copper sulphate with sodium sulphate, and silver nitrate with sodium nitrate. In these cases the metals are deposited directly and not by secondary reaction.

Electrolysis of Cyanide Solutions.—Double cyanides on electrolysis furnish excellent examples of the deposition of a metal through a secondary reaction, and therefore promised to be a fruitful ground for the study of periodicity of the type under discussion. The extreme regularity of the periods is a feature of these experiments, enabling these systems to be used for a quantitative examination.

Mercury potassium cyanide. Mercuric chloride solution was added to 50 c.c. of *N*/2-potassium cyanide until a permanent precipitate was formed, and the solution was then made up to 100 c.c. Electrolysing with a *C.D.* of 9 milliamp./cm.^{2}, excellent periods were obtained from this system, though the amplitude was on the whole considerably less than in the foregoing cases.

The following table shows how, in such an experiment, the amplitude increases to a maximum and then declines, whilst the frequency simultaneously increases (period decreases) and then falls off. It will also be observed that the product of amplitude and period is as constant as could be expected.

Time (mins.).	Amplitude (volts).	Period (secs.).	Product.	Time (mins.).	Amplitude (volts).	Period (secs.).	Product.
0	0·2	0·4	0·08	30	0·3	irreg.	?
3	0·3	0·29	0·087	34	0·3	0·31	0·093
6	0·35	0·24	0·082	36	0·25	0·42	0·105
9	0·4	0·20	0·080	38	0·2	0·5	0·100
12	0·4	0·24	0·096	40	0·1	1·1	0·110
17	0·4	0·19	0·076	42	0·0	∞	—
24	0·35	0·20	0·070				

In this system, the frequency decreases greatly with increasing *C.D.*, as shown by the following table :

Milliamp./cm.^{2}	6·2	8·3	9·2	10·0	12·5	17·7
Period (sec.) ..... *ca.*	0·1	0·2	1·1	5·0	13·0	∞

The frequency was measured by taking the time for 10 successive periods with the aid of a stop-watch. Experience showed that it was possible faithfully to count periods at the rate of 6 per second, although values for higher frequencies were not trustworthy. At the *C.D.* of 6 milliamp./cm.^{2}, the period was judged to be about 0·1 sec. because the movement of the electrometer fibre, as judged by the eye, bordered on to continuity. At a slightly lower *C.D.*, the period was almost certainly rather less than this value.

Taking 0·1 sec. as the smallest duration of a period that has been observed, however, it becomes of interest to calculate the thickness of the film of mercury deposited during that period. Thus, a current of 6·2 milliamp. deposits during 0·05 sec. (mercury is deposited only during each half-period) $3{\cdot}24 \times 10^{-7}$ g. of mercury on an area of 1 cm.^{2}. Assuming that the mercury has its normal density of 13·6, the thickness of the mercury film deposited in each period is $2{\cdot}4 \times 10^{-8}$ cm., *i.e.*, of the order of molecular thickness.

No significance is to be attached to this result in the theory of the subject, for it can be shown that in other cases the thickness of the film formed in each period corresponds to several thousands of molecules; but the important point is that *we have here a case of periodicity in the smallest amount of chemical change.*

At these low *C.D.*'s the amount of chemical change was not sufficient to produce visible periodic evolution of hydrogen, but, nevertheless, the periodicity was easily visible, for the hydrogen bubbles, with which the surface of the cathode became covered, pulsated synchronously with the periodic change of potential. This effect, due to the periodically changing surface tension at the mercury–hydrogen interface as a result of the periodic formation of amalgam, showed itself in a pulsating flattening of the bubbles. The effect was perceptible when the amount of metal deposited in each pulsation could not have exceeded a few molecules in thickness.

Cadmium potassium cyanide. Even better periods were obtained

with a solution made by adding cadmium nitrate to 50 c.c. of $N/2$-potassium cyanide until a permanent precipitate formed, and then making up to 100 c.c. These differed from the periods last mentioned in that considerably higher *C.D.*'s could be used, the amplitude was larger (generally about 0·5 volt), and the frequency *increased* with rise of *C.D.* It is noteworthy that in cyanide solutions the frequency is always high.

The next table shows the change in frequency with increase of *C.D.* In the third column appear values of K, the product of the square of the current into the period, and it will be seen that over a wide range these are remarkably constant, considering the error in measuring such small periods.

Total current (milliamp.).	Period (secs.).	K.	Total current (milliamp.).	Period (secs.).	K.
0·25	2·0	0·125	0·55	0·32	0·097
0·30	0·9	0·082	0·60	0·22	0·080
0·35	0·8	0·098	0·65	0·18	0·076
0·40	0·6	0·096	0·75—1·75	very rapid	—
0·45	0·5	0·101	1·9	0·00	—
0·50	0·4	0·100			

In this case then, the period is inversely proportional to the square of the *C.D.* In this experiment, excess of cadmium cyanide was added so that the composition of the solution should not change during electrolysis. Similar results were obtained whether a cadmium or a platinum cathode was used. Pulsating evolution of hydrogen was visible.

Electrolysis of other Systems.—Periods could not be obtained at the cathode in the electrolysis of solutions of the double cyanides of potassium with copper, silver, iron, nickel, cobalt, and zinc. With the exception of zinc, the hydrogen overvoltage is low, and therefore hydrogen was liberated simultaneously with the metal at all *C.D.*'s, and the zinc potassium cyanide solutions were hydrolysed too readily. Unsuccessful experiments were also carried out with solutions of zinc hydroxide and of lead hydroxide in caustic soda. Poor periods were obtained, however, in the deposition of tin from a solution prepared by adding excess of caustic soda to 25 c.c. of $N/2$-stannous chloride and then making up the volume to 100 c.c. The cathode potential varied between $-1{\cdot}36$ and $-1{\cdot}48$ volts in slow periods of 15 minutes, using a *C.D.* of 7 milliamp./cm.^{2}.

Discussion.

The mechanism of the periodicity will be considered for the typical case of the electrolysis of cadmium potassium cyanide solutions. At low *C.D.*'s potassium ions are discharged, and react with the complex $Cd(CN)_4''$ ions: cadmium is deposited and no

hydrogen appears. But at a certain critical *C.D.* more potassium ions are discharged than can react with the complex ions, so the excess react with the water molecules and hydrogen is evolved. It is evident that the liberated potassium ions dispose of the complex $Cd(CN)_4''$ ions preferentially, and only react with water when these become scarce.

The surprising feature is that after a short interval of time the discharged potassium ions cease to react with water, and again are entirely concerned with the complex ions of cadmium.

This point touches the fundamental question of the cause of periodicity, to which an answer cannot at present be given, research so far having been directed towards discovering the conditions under which periodicity is manifested. A discontinuity must occur at some stage in the mechanism of the reaction. In the experiments on the anode there was some evidence to show that the film as first deposited was unstable and changed suddenly to a stable state. This may also be the case here, although it may be pointed out that the phenomenon is equally explicable on the assumption that a certain critical concentration of the complex ions in the immediate vicinity of the cathode is necessary before reaction takes place.

Whether this be the case or not, it is tolerably certain that the discharged potassium ions react alternately with the complex cadmium anions and with the water molecules. The variation of the period with the inverse square of the *C.D.* finds a ready explanation when one considers the relations in the layer of solution immediately contiguous to the cathode; for, suppose the *C.D.* to be increased n times: then the rate of discharge of potassium ions is increased n times, and the rate of migration of the complex anions from the immediate vicinity of the cathode is increased n times. Since there are n times as many potassium ions discharged, and $1/n$ of the number of $Cd(CN)_4''$ ions to react with, the latter become used up n^2 times as quickly.

It is to be remembered, however, that in the electrolysis of mercury potassium cyanide solutions the period *increased* with rise of *C.D.*; but another factor enters here, for whereas with cadmium potassium cyanide the discharged potassium ion is confronted with the alternatives of reacting with the complex anions or with water molecules, yet another possibility is open in the case of mercury potassium cyanide in that the potassium atom may stay as such in the mercury. Moreover, increase of *C.D.* will stabilise the potassium amalgam, diminishing its tendency to react.

The present work shows that a satisfactory explanation of periodic phenomena in electrolysis must be founded upon as wide a basis as

possible in order to include both anodic and cathodic reactions and the discharge of one or more ions. Elsewhere (Hedges and Myers, "The Problem of Physico-chemical Periodicity," Arnold and Co., 1926) the author has gathered together some reports of earlier experiments of this type. Since these are mostly isolated cases, the earlier investigators proposed a specific mechanism for each. It is now evident that an explanation should be of general applicability. It is hoped by further experiment to eliminate some of the factors which at present lead to ambiguity in interpretation.

Summary.

Periodic changes in the cathode potential and current strength occur between certain limiting current densities during the electrolysis of solutions composed of a mixture of mercuric chloride or mercurous nitrate with solutions of the salts of alkali metals, alkaline earths, or aluminium, and in solutions of mercuric cyanide or cadmium cyanide in potassium cyanide. The phenomenon consists of the alternate deposition of two metals, and has been observed only when one of the metals is deposited through a secondary reaction. The values of the limiting current densities, between which the region of periodicity exists, depend on the relative amounts of the components of the mixed solution. Periodicity has been realised where the amount of metal deposited in each period does not exceed a few molecules in thickness.

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CXLVI.—*Molybdenyl Salts and the Co-ordination Number of Oxygen.*

By WILLIAM WARDLAW and ROBERT LOUIS WORMELL.

ACCORDING to the acid concentration, red or green solutions containing tervalent molybdenum are produced by the electrolytic reduction of molybdenum trioxide in hydrochloric acid. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 173) suggested that the appearance of the green colour might be due to the formation of small masses of molybdenum dichloride which had not been detected chemically,

and that in the red solutions bivalent molybdenum was not produced. The existence of two differently coloured solutions of chromic chloride is well known. Peligot (*Compt. rend.*, 1844, **19**, 783; *Ann. Chim. Phys.*, 1844, **12**, 537) first succeeded in obtaining green crystals of chromium trichloride, $[Cr(H_2O)_4Cl_2]Cl,2H_2O$, by treating the insoluble violet anhydrous trichloride with water in the presence of a small quantity of chromium dichloride. Attempts to isolate isomeric trichlorides of molybdenum have so far been unsuccessful, however.

Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458) conclude from their measurements of potential, that the existence of bivalent molybdenum in the green solutions is highly improbable. In view of the isolation of the complex salts R_3MoCl_6 and R_2MoCl_5,H_2O by the addition of alkali chlorides to solutions of tervalent molybdenum, these authors consider that the colours and properties of the green and red solutions may be due to the varying concentrations of the ions as determined by the equilibria:

$$[MoCl_6]''' \rightleftharpoons Mo''' + 6Cl'; \quad [MoCl_5,H_2O]'' \rightleftharpoons Mo''' + 5Cl' + H_2O;$$
$$[Mo,6H_2O]''' \rightleftharpoons Mo''' + 6H_2O.$$

Nevertheless it is possible to obtain from a green solution of tervalent molybdenum the green oxychloride, $MoOCl,4H_2O$, and from the red solution the brown isomeride, $MoOCl,4H_2O$ (this vol., p. 130). These facts, together with the isolation of the salt $KMoOCl_2,3H_2O$ (this vol., p. 512), furnish strong evidence in favour of the presence of the molybdenyl radical in all solutions of tervalent molybdenum, in accordance with the scheme

$$MoCl_3,xH_2O \rightleftharpoons [MoOCl,4H_2O] + 2HCl + (x-5)H_2O;$$
$$[MoOCl,4H_2O] + H_2O \rightleftharpoons [MoO,5H_2O]' + Cl'.$$

Further proof of the existence of the molybdenyl radical is now received from the preparation of a series of its salts. In addition, the occurrence of a trichloride in the red solution, as postulated by Chilesotti, is confirmed by the isolation of the first *hydrated molybdenum trichloride*, the dark red crystalline substance $MoCl_3,3H_2O$. Previously, the only known trichloride was the insoluble solid prepared by dry methods.

Experimental.

Preparation of Hydrated Molybdenum Trichloride.—A solution of molybdenum trioxide (10 g.) in 400 c.c. of hydrochloric acid (*d* 1·16) was heated on a water-bath for some hours, made up to 600 c.c., and electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 969) until the cathode solution was red. This solution was then evaporated to dryness at 70—80° under dimin-

ished pressure in an air-free flask. The residue was a copper-coloured, crystalline substance, which undoubtedly contained portions of hydrolysed material, and on analysis gave values of the order 1 : 2·5 for the ratio Mo : Cl. 400 C.c. of pure ether, cooled in a freezing mixture of ice and salt, and saturated with dry hydrogen chloride, were drawn into the flask by releasing the vacuum, and the red solution obtained was evaporated to dryness under diminished pressure, whereupon a dark red, crystalline substance separated. In order to ensure the complete conversion of any hydrolysed salt into the normal chloride, this operation was repeated. The substance finally obtained was quickly transferred in an atmosphere of dry carbon dioxide to a desiccator containing phosphoric oxide. The product was extremely hygroscopic, and exceptional precautions had to be taken to exclude moisture.

Analysis.—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, **125**, 1911). The chloride in the filtrate and washings was estimated as silver chloride (Found : Mo, 36·44, 36·48; Cl, 40·77, 41·15; Mo : Cl = 1 : 3·03; 1 : 3·05. $MoCl_3,3H_2O$ requires Mo, 37·44; Cl, 41·49%).

Valency of the Compound.—This was determined as for the oxychloride (*loc. cit.*). One g. of the solid, on direct titration with standard permanganate, required 127·2 c.c. A similar solution, oxidised and passed through the reductor, required 130·2 c.c. The molybdenum is therefore tervalent.

Properties and Reactions of Molybdenum Trichloride.—The substance separates in dark, copper-coloured crystals, very soluble in water, acetone, or cold absolute alcohol, giving intensely red solutions. It rapidly reduces solutions of copper, silver, or mercuric salts. Sodium and ammonium hydroxides give black precipitates, soluble in acids; these are probably the trihydroxide. If potassium chloride is added to a solution of the substance in alcohol, the pink complex chloride, K_2MoCl_5,H_2O, is deposited on warming.

Salts containing the Molybdenyl Radical.—Molybdenyl bromide, like the chloride, has been obtained from a concentrated solution containing tervalent molybdenum by precipitation in acetone (J., 1926, 1592). Practical difficulties precluded the isolation of the corresponding fluoride in a similar way, but it has now been obtained by double decomposition of the oxychloride with ammonium fluoride in an air-free aqueous solution. *Molybdenyl fluoride* was deposited as a buff-coloured, insoluble precipitate the analysis of which agreed with the formula $MoOF,3{\cdot}5H_2O$. The properties of three out of the four possible molybdenyl halides of the general formula $[MoOR,4H_2O]$ can now be compared, and a close resemblance to the alkaline-earth halides is indicated inasmuch as the

solubility of the molybdenyl halides increases with increase in the atomic weight of the halogen atom. Ease of hydrolysis accords with a similar generalisation.

Analysis of Molybdenyl Monofluoride.—The oxyfluoride, suspended in water, was brought into solution by the addition of sodium peroxide. In order to exclude ammonium salts, which have a solvent action on calcium fluoride, the alkaline solution was saturated with hydrogen sulphide, ruby-red thiomolybdate being formed. This was decomposed with dilute hydrochloric acid, and the precipitated sulphide was filtered off, ignited, and weighed as trioxide. The fluoride in the filtrate and washings was estimated as calcium fluoride (Found: Mo, 49·98, 49·60; F, 9·62, 9·45; Mo: F = 1 : 0·97, 1 : 0·96. $MoOF,3{\cdot}5H_2O$ requires Mo, 49·49%).

The univalent molybdenyl radical, MoO, appears to persist in aqueous solution. The oxygen atom seems to be firmly attached to the molybdenum nucleus and the whole behaves like a univalent metal. This conception is supported by the existence of other insoluble molybdenyl salts, such as the benzoate, phosphate, salicylate (this vol., p. 130), and tartrate.

Preparation of Molybdenyl Derivatives.—By double decomposition of the theoretical amounts of molybdenyl monochloride and the alkali salts of benzoic, tartaric, and phosphoric acids, respectively, in air-free aqueous solution, reactions occur in accordance with the equations:

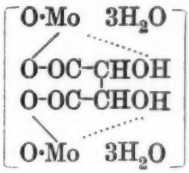
(1) $MoOCl + C_6H_5{\cdot}CO_2Na = C_6H_5{\cdot}CO_2{\cdot}MoO + NaCl.$
(2) $2MoOCl + NaKC_4H_4O_6 = (MoO)_2C_4H_4O_6 + NaCl + KCl.$
(3) $3MoOCl + Na_2HPO_4 = (MoO)_3PO_4 + 2NaCl + HCl.$

These insoluble molybdenyl salts are all buff-coloured and undergo gradual hydrolysis in contact with water. They are best purified by washing with dilute solutions of the corresponding acids. Solutions of sodium oxalate and normal sodium citrate also give well-defined, buff precipitates when they are added to a solution of molybdenyl chloride. These precipitates are probably the corresponding molybdenyl salts.

Analysis. In the following analyses, the phosphate was estimated both as magnesium pyrophosphate and as ammonium phosphomolybdate. The percentages of water correspond to the whole of the hydrogen in the compound and not merely to that in the water of crystallisation. The benzoate was found to be tervalent by titration with permanganate solution. Found for $(MoO)_3PO_4,12H_2O$: Mo, 44·45; PO_4, 14·92. Calc.: Mo, 44·51; PO_4, 14·68%. Found for $C_6H_5{\cdot}CO_2{\cdot}MoO,2{\cdot}5H_2O$: Mo, 33·97; C, 29·95; H_2O, 31·75. Calc.: Mo, 34·53; C, 30·21; $5H_2O$, 32·39%. Found for

$(MoO)_2C_4H_4O_6,6H_2O$: Mo, 40·04; C, 9·96; H_2O, 29·65. Calc.: Mo, 40·00; C, 10·00; $8H_2O$, 30·00%.

These molybdenyl salts can be conveniently symbolised as co-ordination compounds in which the co-ordination number of tervalent molybdenum is six. On using such a formulation for the molybdenyl tartrate, it is seen that the tartrate grouping occupies four co-ordination positions:



The Co-ordination Number of Oxygen.

In dealing with the co-ordination number of multivalent atoms, Werner laid it down that oxygen and other bivalent atoms occupy only one position in the co-ordination sphere. Many examples could be quoted to support this view, but in other cases its acceptance involves assigning to an element an odd co-ordination number in circumstances which appear unlikely. Chromium, well known for the stability of its six-point system, forms salts of the type $[CrOCl_4]R$, in which, on Werner's view, the co-ordination number of chromium must be five. The same co-ordination number would be assigned to the central atom in the compounds $WOCl_4$, $MoOF_4$, $[VOF_4]K_2$, and $[NbOCl_4]C_5H_6N$. Nevertheless, the possibility that oxygen may occupy two positions, and thereby give rise to a co-ordination number of six, should not be overlooked. Electronic theories of valency have clearly demonstrated the essential difference between oxygen atoms occupying one or two positions in the co-ordination sphere. When an oxygen atom is attached to the central atom by a semipolar double bond, it occupies one co-ordination position, and when attached by a double bond, two. The resolution of the amine and phosphine oxides with the configuration $[R_1R_2R_3N\rightleftharpoons O]$ is explained most readily by supposing that the four units are tetrahedrally distributed round the central nitrogen or phosphorus atom, and that the oxygen bound to the central atom by a semipolar double bond occupies one position. Again, the optical activity associated with the sulphinates and sulphoxides (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, J., 1926, 2079) is satisfactorily explained by assigning to these substances a configuration $[O\rightleftharpoons SR_1R_2]$ in which the oxygen occupies one position in the tetrahedral structure.

Whilst the double link (two co-ordination positions) is required

to avoid improbable co-ordination numbers in many compounds, such as those previously mentioned, it is especially necessary to explain the behaviour of carbon. If the carbonyl group were $C\rightleftharpoons O$, the carbon would be tri-co-ordinated or tervalent. The results of Sugden and his colleagues (J., 1925, **127**, 1525) show, however, that carbon never forms a semipolar link with oxygen. This view is also supported by the conclusion from *X*-ray analysis, that the three oxygen atoms in the CO_3'' ion lie in the same plane with the carbon (W. L. Bragg, *Proc. Roy. Soc.*, 1914, *A*, **89**, 468), because with the tetrahedral model for carbon, the three atoms in $O{=}C{<}^{O}_{O}$ would lie in a plane with the carbon, whereas in $O{\leftarrow}C{<}^{O}_{O}$ they would lie out of a plane as they do in $O{\leftarrow}S{<}^{O}_{O}$. On the basis of the *X*-ray result that the angle between the valencies to any two oxygen atoms in the CO_3'' and NO_3' ions is 120°, whereas that between the two singly-linked atoms might be expected to be 109° 28′, Lowry has assigned (*Chemistry and Industry*, 1927, 78) a trigonal orientation to the oxygen atoms around the central atom of the anion and concludes "that it is clear that van 't Hoff's tetrahedral model of the carbon atom now has a rival." It must, however, be borne in mind that "the tetrahedron representing a carbon atom is approximately regular only when the carbon atom is attached to four atoms of a similar kind" (Ingold, J., 1921, **119**, 306). Thus the tetrahedral angle must be modified in every case where the four linkings are not exactly equivalent, and on the Thorpe–Ingold theory this angle must be increased by the double link to the third oxygen. Moreover, since the two singly-linked oxygen atoms are negatively charged, they must repel each other and give rise to a greater value for the angle between them. It seems doubtful, therefore, whether any modification of van 't Hoff's conception is necessary or justified.

A suitable interpretation of the structure of those molybdenyl salts, such as $[MoOR,3{\cdot}5H_2O]$, whose water content is less than would be anticipated from a co-ordination number of six for the molybdenum, would be to consider these compounds to be the result of the equilibrium

$$H_2O + [MoOR,3H_2O] = [MoOR,4H_2O]$$

where, in one case, the oxygen occupies one position, and in the other, two positions in the co-ordination sphere.

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CXLVII.—*The Crystal Structure of Quinol. Part II.*

By WILLIAM AUGUSTUS CASPARI.

In a previous paper (J., 1926, 2944), some account was given of the X-ray examination of that trigonal modification of quinol which crystallises from aqueous solutions, and may be called α-quinol. There are, however, at least two other polymorphs, one of which, here referred to as γ-quinol, is monoclinic and has been known for a long time.

β-*Modification of Quinol.*—It was found in the course of the present investigation that when quinol is deposited from methyl-alcoholic solution at the ordinary temperature, it crystallises in hexagonal

FIG. 1.

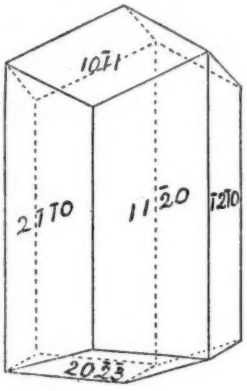
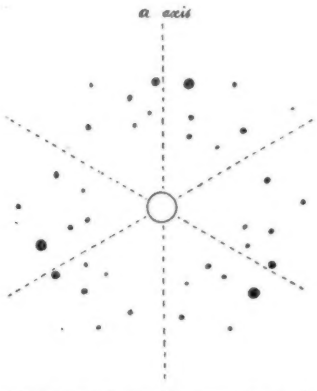


FIG. 2.



β-Quinol, Laue diagram through (0001), *as at distance* 1·75 *cm.*

prisms resembling those of α-quinol at first sight, but belonging to a different subdivision of the trigonal system. This modification may be termed β-quinol. The crystals consist of prisms capped, not by rhombohedra, but by trigonal pyramids both of the first order, with a well-marked hemimorphism along the *c* axis. The typical crystal habit is shown in Fig. 1. In general, the crystals are not so excessively acicular as those of α-quinol, the prisms tending to be fairly thick in relation to their length. The density, 1·31, and m. p., 166°, are somewhat lower than those of α-quinol.

From its external symmetry, β-quinol must be placed either in the ditrigonal-pyramidal (tourmaline) or in the trigonal-polar (sodium periodate) class. Definite evidence in favour of the latter class is afforded by Laue photographs through the (0001) plane. A diagrammatic reproduction, in which the size of the spots is an indication of their intensity, is given in Fig. 2. It will be observed that,

whilst trigonal axial symmetry about c is well brought out, symmetry about planes parallel to c is absent. The latter planes being, apart from the triad axis, the characteristic symmetry elements of the tourmaline class, β-quinol can only possess the lower symmetry of the sodium periodate class, space-groups C_3^1 to C_3^4.

Under X-ray examination, the crystals reflect considerably better than those of α- or γ-quinol. Rotation photographs about axes normal to (0001), (11$\bar{2}$0), and (10$\bar{1}$0) gave the following results:

Cell-dimension	c	(mean of	7	spots on	2	layer-lines):	c	=	5·53 Å.
„	„	a	(	„	8	„	5	„):	a	= 16·25 Å.
„	„	$a\sqrt{3}$	(	„	10	„	9	„):	$a\sqrt{3}$	= 28·12 Å.
							whence	a	= 16·24 Å.

In the c photograph the first layer-line is the strongest both in number and in intensity of spots. In all three photographs equally, (30$\bar{3}$0) and (22$\bar{4}$0) give the strongest reflexions in the prism zone, whilst among pyramidal forms (13$\bar{4}$1) and (12$\bar{3}$1) stand out by the intensity of their reflexions.

Oscillation photographs about c through 10° including the main prism face (11$\bar{2}$0) showed lines at 8·1 Å., 4·05 Å., and 2·7 Å. Since $d_{11\bar{2}0}$ is thus $a/2$, a hexagonal lattice, as in the case of α-quinol, is indicated.

For the number of molecules per cell we have

$$n = \frac{5{\cdot}53 \times (16{\cdot}25)^2 \times \sqrt{3}/2 \times 1{\cdot}31}{110 \times 1{\cdot}65} = 9{\cdot}1,$$

i.e., 9 molecules. The maximum number of lattice-units required for the symmetry of a trigonal-polar crystal is three. Consequently each unit contains the substance of three molecules, three such units going to the cell. The three molecules in each unit have no symmetry, either in each molecule separately or in the three as a group. We have here, then, another such case of triple crystallographic association as in α-quinol (*loc. cit.*). In the present instance, three of the composite lattice-units are arranged about triad axes of symmetry throughout the crystal; but neither the lattice-units nor their orientations in the cell provide a plane of symmetry normal to the c axis. The space-group of β-quinol, finally, appears to be C_3^1.

γ-Modification of Quinol.—When quinol is crystallised by sublimation, a small proportion of the mainly acicular sublimate takes the form of thin leaflets having the contours of an acute-angled rhomb. Lehmann (*Z. Kryst. Min.*, 1877, **1**, 43) found this polymorph, or γ-quinol, to be monoclinic-prismatic, with β = 107°, the flat face being (001) and the prism contours {11$\bar{1}$}. The present X-ray results entirely confirm this interpretation.

In density, 1·325, and m. p., 169°, the crystal resembles α-quinol

rather than β-quinol. The leaflets frequently undergo spontaneous distortion within a few hours of being prepared, and gradually become opaque in the course of a few weeks; hence this modification of quinol does not appear to be stable at the ordinary temperature.

Rotation-photographs about the axes set up by Lehmann provided the following data:

Cell-dimension along	*a*	(mean of	6	spots on	4	layer-lines):	*a* =	13·24 Å.
,,	,,	*b*	(,,	5	,,	2	,,	):	*b* =	5·20 Å.
,,	,,	*c*	(,,	6	,,	3	,,	):	*c* =	8·11 Å.

The number of molecules per cell is given by

$$n = \frac{13{\cdot}24 \times 5{\cdot}20 \times 8{\cdot}11 \times \sin 73^\circ \times 1{\cdot}325}{110 \times 1{\cdot}65} = 3{\cdot}95,$$

i.e., 4 molecules. In the rotation photographs, the strongest reflexion was from (002), with weaker ones from (004) and (006), and none from odd orders of the base. Reflexions of more than average intensity were also given by (001), (012), and (200). No halvings of (*hkl*) planes could be traced, but (010) is halved, and (*hol*) planes in which either *h* or *l* is odd. It may be inferred, therefore, that the γ-quinol crystal falls into space-group C_{2h}^5, and is built up on the simple lattice Γ*m*.

The proximate data for the crystal structure of quinol are thus at hand, and further methods of investigation will lead to an understanding of the arrangement of atoms and molecules in the several crystals. It is seen that although quinol, like most organic substances, can crystallise in unimolecular units and monoclinic symmetry (γ-quinol), yet it tends in its stabler forms (α- and β-quinol) to associate in termolecular units and to crystallise in the trigonal system. In its trigonal modifications, quinol, like the trigonal crystals quartz (Bragg and Gibbs, *Proc. Roy. Soc.*, 1925, *A*, **109**, 405) and carborundum (Ott, *Z. Krist.*, 1926, **63**, 1), shows a tendency to preserve certain simple axial relations in its passage from one polymorph to another. Thus the *c* axes of α- and β-quinol are almost the same, whilst the respective *a* axes are nearly in the ratio of 4 to 3. The better reflecting power of the planes in β-quinol than of those in α- and γ-quinol is another datum which, although its exact bearing is not clear at present, must play its part in the ultimate interpretation of these crystals.

The author desires to thank Sir William Bragg, F.R.S., for the interest he has taken in this work and for his valuable suggestions.

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CXLVIII.—*A Study of the Chemiluminescence of Phosphorus Vapour.*

By Edmund John Bowen and Edward George Pells.

The following work on the luminescence of phosphorus vapour in oxygen was an attempt to compare the number of molecules reacting chemically with the number emitting visible light during the process. The radiation emitted by glowing phosphorus vapour consists of a continuous band extending throughout the visible region (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235), a band spectrum in the near ultra-violet (Emeléus and Downey, J., 1924, **125**, 2491), and very probably wave-lengths less than 1800 Å. capable of ozonising oxygen. The distribution of energy in these different regions is not known.

The number of molecules producing light during the phosphorescence was determined by measuring photographically the number of quanta of light emitted. One part of a panchromatic plate was exposed to the glow and another part to the light from a tungsten filament lamp passed through a copper sulphate–ferrous sulphate filter to remove infra-red radiation. Equality of blackening on the plate was taken to indicate equality of luminous energy falling on the plate in the two cases. This assumption depends on the similarity of the distribution of energy in the visible region of the spectrum of glowing phosphorus vapour and of the filtered light from the tungsten lamp. It was shown to be justified to a sufficient degree of accuracy by photographs of the two sources of light through glass filters supplied by Messrs. Chance Bros. The following table gives the results:

Transmission region of glass filter (Å.)	7000—5300	6000—4800	4900—4000	3800—3200
Relative blackening for tungsten lamp	4	1	2	0
Relative blackening for phosphorus glow	4	2	1	0

Within a factor of less than 2, equal blackening therefore seemed to indicate equal quantities of energy incident on the plate from the two light sources.

The energy per second in the light from the tungsten lamp was measured with a thermopile calibrated in the usual way with a Hefner lamp. When the panchromatic plate was exposed to the light it was placed much farther away than the thermopile, and the incident energy was calculated by the inverse-square law. The same law was also used, although it is only approximate because of the large size of the light source, in calculating the total luminous

energy radiated by the glowing phosphorus vapour from the blackening on the plate placed a known distance away.

In the first series of experiments the white phosphorus was contained in a thin layer, obtained by distillation in a high vacuum, on one half of the inside of a glass bulb about 2 cm. in diameter, which was immersed in water at a suitable temperature. The panchromatic plate was placed a short distance above the bulb. The bulb was connected to a larger bulb to act as a reservoir and to a McLeod gauge. Pure oxygen was admitted to the reservoir and gauge, the initial pressure measured, and the gas allowed to enter the phosphorus bulb. The glow filled the whole bulb, indicating that the reaction was between the oxygen and the phosphorus vapour (Rayleigh, *Proc. Roy. Soc.*, 1924, *A*, **106**, 1). When the reaction had proceeded for a definite time the residual pressure was measured. The glow seemed to remain fairly constant during each experiment, although in different experiments the rate of oxygen absorption varied greatly, apparently depending on the rate of volatilisation of the phosphorus as controlled by variation in a thin crust of oxide on the surface of the solid.

The following are the mean results obtained in three series of experiments:

1. Initial oxygen pressure = 5·17 mm.

Blackening on plate by phosphorus glow corresponds (from tungsten lamp–thermopile calibration) to $1{\cdot}76 \times 10^{-6}$ cal. per sq. cm.

Fraction of glow received on 1 sq. cm. of plate = $1/16\pi$ (approx.). Therefore total luminous energy emitted as phosphorescence = $8{\cdot}85 \times 10^{-5}$ cal.

If $h\nu = 8{\cdot}3 \times 10^{-20}$ cal. be taken as a mean energy of a quantum in the visible region, number of quanta emitted during the glow = $1{\cdot}06 \times 10^{15}$.

Number of molecules of oxygen absorbed

$$= 6 \times 10^{23} \times (\text{vol. of apparatus})(\text{cm. } O_2 \text{ absorbed})/76 \times 23{,}000$$
$$= 3{\cdot}42 \times 10^{19}.$$

The final product of oxidation is phosphoric oxide, produced as a result of a series of consecutive reactions; of these we may assume that only one emits light, and that it probably involves only one molecule of oxygen. If this is so, one-fifth of the oxygen molecules reacting may be taken as the number concerned in the luminescent stage.

If r represents the ratio of the number of such molecules to the number of quanta of light emitted, we have

$$r = 6{\cdot}8 \times 10^{18}/1{\cdot}06 \times 10^{15} = 6{\cdot}4 \times 10^{3}.$$

2. Initial oxygen pressure = 3·5 mm.
Number of quanta emitted during the glow = 4×10^{14}.
Total number of molecules of O_2 absorbed = $3{\cdot}4 \times 10^{19}$.

$$r = 6{\cdot}8 \times 10^{18}/4 \times 10^{14} = 1{\cdot}7 \times 10^{4}.$$

3. Initial oxygen pressure = 1·18 mm.
Number of quanta emitted during the glow = $1{\cdot}42 \times 10^{15}$.
Total number of molecules of O_2 absorbed = $2{\cdot}4 \times 10^{19}$.

$$r = 4{\cdot}8 \times 10^{18}/1{\cdot}42 \times 10^{15} = 3{\cdot}4 \times 10^{3}.$$

An important source of error in these experiments was the possible reaction of some of the oxygen with the solid phosphorus present, *i.e.*, the combination might not take place wholly in the vapour phase. To eliminate this, another series of experiments was performed. Phosphorus was vaporised at about 25° in a current of pure dry nitrogen and the gas passed into a small warmed bulb into which oxygen was allowed to leak. The glow in the vessel was photographed as before. To secure greater accuracy of comparison a neutral optical wedge was used in front of the plate for the exposure to the calibrated lamp, the times of exposure to the glow and to the lamp being the same. The amount of oxygen reacting with the phosphorus vapour was found by drawing the gases into a small vessel cooled in carbonic acid snow, and weighing the oxide deposited. The results of four experiments are given below:

Energy from lamp = $2{\cdot}5 \times 10^{-6}$ cal. per sec. per sq. cm. of plate.
Fraction of glow received on 1 sq. cm. of plate = 0·05.

Ratio of energy: glow/lamp.	Quanta emitted as luminescence per sec.	P_4O_{10} collected in 30 mins. (g.).	Molecules produced per sec.	Ratio Mols./Quanta.
1/10	6×10^{13}	0·121	$13{\cdot}1 \times 10^{16}$	$2{\cdot}18 \times 10^{3}$
1/8	$7{\cdot}5 \times 10^{13}$	0·126	$13{\cdot}6 \times 10^{16}$	$1{\cdot}81 \times 10^{3}$
1/10	6×10^{13}	0·129	$13{\cdot}9 \times 10^{16}$	$2{\cdot}32 \times 10^{3}$
1/12	$5{\cdot}2 \times 10^{13}$	0·121	$13{\cdot}1 \times 10^{16}$	$2{\cdot}52 \times 10^{3}$

These results are in agreement with those obtained by the previous method, and indicate that at least one in 2000 of the P_4 molecules undergoing oxidation emits a quantum of visible light. The agreement between the two series of experiments, however, must be viewed in the light of the assumptions made in the first series and of the possible effect of nitrogen on the glow in the second. As the light emitted is partly obscured by the cloud of solid oxide formed, the proportion of luminescent molecules is probably greater; also the number of molecules emitting ultra-violet light is not given by these experiments. Rayleigh (*loc. cit.*) has shown that the oxidation of phosphorus vapour with luminescence is a catalytic phenomenon occurring at the surface of solid oxide particles. The results of this paper on the fairly large proportion of luminescent molecules in the

oxidation, when account is taken of the losses of light and of ultra-violet light emitted, seem to be most simply interpreted by assuming that the glow of phosphorus is a chemiluminescence of the type described by Kautsky (*Trans. Faraday Soc.*, 1926, **21**, 591). In his experiments, dyes adsorbed on a surface of siloxen undergoing oxidation were excited to emit their fluorescent spectrum as chemiluminescence. If the theory is extended to the case of phosphorus, it must be assumed that oxidation at the surface of solid particles of an oxide excites to luminescence adsorbed molecules of some other oxide. A large number of chemiluminescence phenomena are associated with reactions on solid particles, two well-defined cases being the oxidation of phosphorus and the oxidation of the dithiocarbonic acid esters. The curious phenomenon of the glow and explosion of so-called pure phosphine and oxygen mixtures when the pressure is suddenly reduced (van 't Hoff, " Studies in Chemical Dynamics," 1896), which has been shown by Emeléus (J., 1925, **127**, 1362) to emit the spectrum of glowing phosphorus, can only be reasonably explained by the catalytic effect of solid hydrogen phosphides or other particles deposited by the sudden cooling.

An interesting calculation is the " efficiency " of the oxidation of phosphorus as a light producer. The heat of formation of 1 g.-mol. of P_4O_{10} is 740,000 cals. A g.-mol. quantum of green light is 50,000 cals., whence, during phosphorescence,

$$\text{Energy of light/Total energy} = 3 \times 10^{-5}.$$

This is not a very high efficiency when compared with that for a candle, 10^{-2}; an electric lamp, 10^{-1}; or a mercury-vapour lamp, 0·5.

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CXLIX.—*αβ-Dichloro-β-bromovinyl Ethyl Ether.*

By ISOBEL AGNES SMITH.

BY brominating αβ-dichlorovinyl ethyl ether and then heating the addition product, Crompton and Triffitt (J., 1921, **119**, 1874) obtained chlorobromoacetyl chloride. If the addition product is not heated but is treated at once with alcoholic potash, *αβ-dichloro-β-bromovinyl ethyl ether* is obtained in good yield :

$$\text{CHCl:CCl·OEt} + \text{Br}_2 = \text{CHClBr·CClBr·OEt}.$$
$$\text{CHClBr·CClBr·OEt} + \text{KOH} = \text{CClBr:CCl·OEt} + \text{KBr} + \text{H}_2\text{O}.$$

This ether resembles αβ-dichlorovinyl ethyl ether in its reactions towards ethyl alcohol and phenol (compare Crompton and Vander-

stichele, J., 1920, **117**, 691). The reactions, however, take place less readily, considerable heating being necessary to induce the ether to react. The reactions with ethyl alcohol, phenol, β-naphthol, and quinol were studied and in each case gave rise to the corresponding ester :

$$CClBr{:}CCl{\cdot}OEt + R{\cdot}OH = CHClBr{\cdot}CO_2R + EtCl.$$

The ether was also found to resemble αβ-dichlorovinyl ethyl ether in its reactions with acids, concentrated sulphuric acid, glacial acetic acid, and benzoic acid being selected as typical acids for the comparison. In each case ethyl chlorobromoacetate was obtained and, in the latter two cases, the acid chlorides of the reacting acids :

$$CClBr{:}CCl{\cdot}OEt + R{\cdot}CO_2H = CHClBr{\cdot}CO_2Et + R{\cdot}COCl.$$

In the experiment with glacial acetic acid a secondary reaction took place on prolonged heating. No acid chloride could then be detected, but in addition to ethyl chlorobromoacetate considerable quantities of ethyl acetate and chlorobromoacetic acid were obtained.

When brominated, αβ-dichloro-β-bromovinyl ethyl ether gave *αβ-dichloro-αββ-tribromodiethyl ether*, which on exposure to moist air readily lost its halogen and passed into oxalic acid. On being heated in the absence of moisture, the ether was converted into chlorodibromoacetyl chloride, a reaction which also took place slowly on allowing the compound to remain in a sealed tube for several weeks at the ordinary temperature.

$$CClBr_2{\cdot}CClBr{\cdot}OEt \longrightarrow CClBr_2{\cdot}COCl + EtBr.$$

Chlorine appeared to act on αβ-dichloro-β-bromovinyl ethyl ether in a similar manner.

EXPERIMENTAL.

αβ-Dichloro-β-bromovinyl Ethyl Ether.—To 100 g. of αβ-dichlorovinyl ethyl ether (Crompton and Vanderstichele, J., 1920, **117**, 691), cooled in a freezing mixture of ice and salt, 34 c.c. of bromine were run in slowly, the coloration then being permanent. The product was added to a solution of potassium hydroxide (60 g. of KOH, 40 c.c. of water, 310 c.c. of absolute alcohol) and, after ½ hour, sodium bromide having separated, the mixture was poured into 2 l. of water. The oil thus produced was washed with water, dried over soda-lime, and fractionally distilled, 100 g., b. p. 172—177°, being obtained. *αβ-Dichloro-β-bromovinyl ethyl ether* is a colourless liquid, b. p. 177°/754 mm., $d_4^{20°}$ 1·6565, $d_4^{26°}$ 1·6478, $d_4^{30°}$ 1·6422, $n_D^{17·5°}$ 1·50427; whence $[R_L]_D^{17·5°}$ 39·24 (Found : Cl, 32·1; Br, 36·2. $C_4H_5OCl_2Br$ requires Cl, 32·2; Br, 36·3%).

Ethyl alcohol, phenol, and β-naphthol, by interaction with this ether, gave ethyl, phenyl, and β-naphthyl chlorobromoacetate, respectively, the product being identified in each case by its physical properties and by analysis. Quinol gave quinol bischlorobromoacetate, m. p. 122—123°. Concentrated sulphuric acid gave ethyl chlorobromoacetate, whereas acetic acid and benzoic acid yielded ethyl chlorobromoacetate together with acetyl chloride and benzoyl chloride, respectively, the acid chlorides being identified by conversion into the corresponding anilide and amide.

Action of Bromine on αβ-Dichloro-β-bromovinyl Ethyl Ether.—The ether (80 g.) was brominated at 0°, *αβ-dichloro-αββ-tribromodiethyl ether* separating as a solid. After recrystallisation from light petroleum, this ether (yield 82 g.) had m. p. 28—29°, $d_4^{31°}$ 2·2297, $d_4^{40°}$ 2·2138, $n_D^{34°}$ 1·56833; whence $[R_L]_D^{34°}$ 55·88 (Found : Cl, 18·8; Br, 63·9. $C_4H_5OCl_2Br_3$ requires Cl, 18·7; Br, 63·2%). It is readily soluble in the cold in acetone, alcohol, carbon tetrachloride, benzene or xylene, and insoluble in cold or hot water.

Action of Heat on αβ-Dichloro-αββ-tribromodiethyl Ether.—The ether was heated at about 60° in a hard glass tube drawn out to a fine capillary. Ethyl bromide was evolved and the ether changed almost quantitatively into chlorodibromoacetyl chloride. This was identified by conversion into chlorodibromoacetamide, which, mixed with an authentic specimen, melted at 127—128°. The acid chloride was further characterised by conversion into the *anilide*, which, after crystallisation from aqueous alcohol, melted at 102—103° (Found : N, 4·4. $C_8H_6ONClBr_2$ requires N, 4·3%).

Action of Chlorine on αβ-Dichloro-β-bromovinyl Ethyl Ether.—Dry chlorine was readily absorbed by αβ-dichloro-β-bromovinyl ethyl ether at 0°, but the product could not be obtained crystalline, nor any uniform material by distillation under reduced pressure. On exposure to moist air, the product was largely converted into oxalic acid; and when it was heated at 60° for several hours in a tube drawn out to a capillary, dichlorobromoacetyl chloride (identified by conversion into dichlorobromoacetamide) was formed. These results indicated the presence of ααββ-tetrachloro-β-bromodiethyl ether, but this could not be isolated.

Molecular Refractivities.—The molecular refractivity of αβ-dichloro-β-bromovinyl ethyl ether, obtained from the observed refractivity by the Lorenz and Lorentz formula, is slightly lower than that calculated by means of Eisenlohr's atomic refractivities, and that of αβ-dichloro-αββ-tribromodiethyl ether is somewhat higher. The refractivities of the allied compounds αβ-dichlorovinyl ethyl ether and αββ-trichlorovinyl ethyl ether were therefore determined for comparison; the former has $d_4^{20°}$ 1·2037, $d_4^{25°}$ 1·1972, $d_4^{30°}$ 1·1909,

$n_D^{16\cdot5°}$ 1·45584, and the latter has $d_{4°}^{20°}$ 1·3409, $d_{4°}^{25°}$ 1·3343, $d_{4°}^{20°}$ 1·3280, $n_D^{16°}$ 1·47551.

	$[R_L]_D$. Found.	Calc.	Diff.
αβ-Dichloro-β-bromovinyl ethyl ether	39·24	39·35	−0·11
αβ-Dichlorovinyl ethyl ether	31·71	31·582	+0·13
αββ-Trichlorovinyl ethyl ether	36·73	36·449	+0·28
αβ-Dichloro-αββ-tribromodiethyl ether	55·88	55·34	+0·54

The somewhat anomalous behaviour of αβ-dichloro-β-bromovinyl ethyl ether may be connected with the *cis-trans* isomerism which it should exhibit, but attempts to isolate the isomerides from the product prepared as above were not successful.

The author desires to express her thanks to Mr. Holland Crompton for much advice and criticism.

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CL.—*The Basic Character of the Acetoxylidides and its Influence on the Course of their Substitution.*

By HERBERT ERIC DADSWELL and JAMES KENNER.

IN continuance of earlier work on substituted diphenic acids, it was desired to examine diphenyl-2 : 6 : 2′ : 6′-tetracarboxylic acid (Mayer, *Ber.*, 1911, **44**, 2301) and its derivatives. During the preparation of the *m*-2-xylidine required for this purpose, an interesting property of its acetyl derivative was observed. In one experiment, for example, in which aceto-*m*-2-xylidide had been boiled with 6 litres of concentrated hydrochloric acid, 440 g. crystallised when the solution was diluted with an equal bulk of water and cooled, but a further 200 g. were precipitated when the liquor was neutralised. Although such treatment with hydrochloric acid is a very usual method of purifying the compound, its very noteworthy basicity seems completely to have escaped notice by previous workers and is not mentioned in the recent paper of Morgan and Hickinbottom (*J. Soc. Chem. Ind.*, 1926, **45**, 2228). It is in fact sufficiently pronounced to permit of the preparation of salts by mixing the acetyl derivative with moderately concentrated mineral acids. The *hydrobromide* and *nitrate*, thus obtained, are stable substances, but the hydrochloride gradually loses hydrogen chloride on exposure to the air. Characteristically crystalline, stable hydrobromides of aceto-*m*-4-, -*p*-, -*o*-3-, and -*o*-4-xylidides and of acetomesidide have been similarly prepared and analysed, so that it would appear that

the basic properties of these acetyl derivatives are due at least in part to the general effect of the introduction of methyl groups into the molecule, irrespective of their orientation. Although salts of acetanilide have been prepared, they are unstable in presence of water (Noelting and Weingärtner, *Ber.*, 1885, **18**, 1340; Wheeler, Barnes, and Pratt, *Amer. Chem. J.*, 1897, **19**, 676; Knorr, *Annalen*, 1888, **245**, 375).

Whilst it will be of interest to pursue this matter further in a general manner, it has been first followed up more particularly in connexion with the original purpose of these experiments, namely, the formation of substitution derivatives of *m*-2-xylidine. Previous workers had shown that bromination of the base in glacial acetic acid solution occurs, as might be expected, in the 5-position, but that 4-nitro-derivatives are obtained from both the base and its acetyl derivative (Noelting and Stoecklin, *Ber.*, 1891, **24**, 568; Noelting, Braun, and Thesmar, *Ber.*, 1901, **44**, 2259). Our observations on salt formation suggested that this might be the factor determining the course of nitration, and the idea gained credence when it was found that bromination of the acetyl derivative in chloroform solution occurs in the 5-position, in glacial acetic acid solution chiefly in the 5- but also, as Noelting and Pick had observed, in the 4-position, and in hydrobromic or sulphuric acid suspension very largely, if not solely, in the 4-position. We therefore expected to be able to obtain 5-nitro-*m*-2-xylidine by the use of m-*nitrobenzo*-m-2-*xylidide*. Although, however, this compound is not noticeably basic in character, it also yielded a 4-*nitro*-derivative, whether sulphuric acid were present or not. This result perhaps does not entirely exclude salt formation as a contributory factor in the behaviour of the acetyl derivative, but it is clearly not a necessary one. This became still more apparent when it was found that bromination of the free base in presence of hydrobromic acid, as of acetic acid, occurs in the 5-position.

The complexity of the problem was not diminished when, for purposes of comparison, the behaviour of *m*-4-xylidine was considered. Although the directive influences in this compound and its derivatives would be expected to accord very closely with those in their 2-isomerides, the two series are not in all respects analogous in behaviour. Whilst, for example, bromination of the base in glacial acetic acid solution occurs in the 5-position (Noelting, Braun, and Thesmar, *loc. cit.*), its acetyl derivative is attacked in the 6-position (Genz, *Ber.*, 1870, **3**, 225; Noelting, Braun, and Thesmar, *loc. cit.*). Not only have we confirmed the latter observation, but we have also found that the result is the same in chloroform solution, as well as in presence of hydrobromic acid. Again, not only the

base, but also its acetyl derivative, in presence of sulphuric acid suffers nitration in the 6-position, whereas nitric acid alone converts the acetyl derivative into 5-nitroaceto-*m*-4-xylidide. By similar variations of experimental conditions, 5- or 6-*nitro*-derivatives are obtained from m-*nitrobenzo*-m-4-*xylidide*, but, as already mentioned, this is not applicable to the 2-isomeride.

There would seem to be no very obvious way of embracing these results within one generalisation, so that detailed discussion may be reserved until the behaviour of the other xylidines has been examined. But it would seem that even in the commonest forms of substitution, as well as in mercuration (Coffey, J., 1925, **127**, 1029; Burton, Hammond, and Kenner, J., 1926, 1802), the nature of the entering substituent requires consideration. Also it is clear that the widely accepted doctrine of salt formation as a determining factor on the course of the nitration of amines is at least not unreservedly applicable to every case.

EXPERIMENTAL.

On the addition of hydrobromic acid, b. p. 126°, to aceto-*m*-2-xylidide, the compound passed into solution, but almost immediately small needles of the *hydrobromide* separated (Found: N, 6·0; equiv., 245. $C_{10}H_{13}ON,HBr$ requires N, 5·7%; equiv., 244). By dilution with water a clear solution was obtained, from which the original acetyl derivative was precipitated on the addition of alkali. (This observation applies equally to the other salts to be described.) In each case the salt was prepared for analysis by thoroughly draining it on porous earthenware and finally drying it in a vacuum over solid potassium hydroxide for 12 hours. The *nitrate* was obtained in hexagonal prisms by use of a mixture of nitric acid (*d* 1·42) with three volumes of water (Found: N, 12·4; equiv., 226·3. $C_{10}H_{13}ON,HNO_3$ requires N, 12·4%; equiv., 226). The sulphate also was prepared, but it could not be completely freed from sulphuric acid. *Aceto*-m-4-*xylidide hydrobromide* formed minute prisms (Found: equiv., 247). *Aceto*-m-4-*xylidide hydrochloride* separated from concentrated hydrochloric acid in plates (Found: equiv., 202. $C_{10}H_{13}ON,HCl$ requires equiv., 199·5). *Aceto*-p-*xylidide hydrobromide* forms hexagonal leaflets (Found: equiv., 243), and *aceto*-o-3-*xylidide hydrobromide* rectangular plates (Found: equiv., 247). *Aceto*-o-4-*xylidide hydrobromide*, prismatic crystals, is hydrated (Found: equiv., 261). Acetomesidide was prepared by Feith and Davies (*Ber.*, 1891, **24**, 3546) from the oxime of methyl mesityl ketone, but it can also be easily obtained by boiling a solution of the base (4 g.) in benzene (10 c.c.) with acetic anhydride (4 c.c.). It also furnished a stable *hydrobromide*, which crystallised

in small, hexagonal prisms (Found: equiv., 256. $C_{11}H_{15}ON,HBr$ requires equiv., 258).

Substitution in m-2-*Xylidine and its Derivatives.*

Bromination Experiments.—For the purpose of these experiments, authentic 4-bromo-*m*-2-xylidine was prepared by Noelting, Braun, and Thesmar's method (*Ber.*, 1901, **34**, 2261). In this connexion, 4-nitro-*m*-2-xylidine was conveniently converted into 2 : 4-dinitro-*m*-xylene by oxidising a suspension of the base (10 g.) in ice-water (375 g.) with the paste prepared from potassium persulphate (50 g.) and sulphuric acid (100 g.), and oxidising the resulting crude nitroso-derivative with nitric acid (*d* 1·48; 75 c.c.) at 40—45°. Reduction of the dinitro-compound by ammonium sulphide as prescribed by the above authors is very slow and is much more effectively achieved by gradual addition of a solution prepared from crystallised (the commercial product gives less satisfactory results) sodium sulphide (7·5 g.), sulphur (2 g.), and water (30 c.c.) to a boiling suspension of the dinitro-compound (5·8 g.) in water (200 c.c.). Furthermore, the use of tin and hydrochloric acid (17 c.c.) was found more satisfactory for reduction of 4-bromo-3-nitro-*m*-xylene (8 g.) than the procedure adopted by Noelting, Braun, and Thesmar.

(*a*) When a solution of aceto-*m*-2-xylidide (2 g.) and bromine (2 g.) in chloroform (10 c.c.) was left in contact with iron wire at the ordinary temperature for 12 hours, the product was 5-bromoaceto-*m*-2-xylidide (Found: N, 5·85%), which was obtained in the pure condition (m. p. 194—195°) after one crystallisation from alcohol.

(*b*) On the other hand, if the acetyl derivative and bromine in the same proportion were allowed to interact at the ordinary temperature for ½ hour in glacial acetic acid (20 c.c.), the 5-bromo-derivative was obtained in the pure condition only after two crystallisations from dilute alcohol, and fractions of lower melting point were recovered from the mother-liquors. These were not further investigated in view of the definite statement of Noelting, Braun, and Thesmar (*loc. cit.*, p. 2262) that the 4-bromo-derivative is also produced under such conditions.

(*c*) The finely ground suspension resulting from the mixture of aceto-*m*-2-xylidide (12 g.) with hydrobromic acid (b. p. 126°; 120 c.c.) was first converted at the ordinary temperature by addition of bromine (12 g.) into a pasty mass, which resolidified after some time. The product collected after 12 hours was 4-bromoaceto-*m*-2-xylidide (12 g.), which was obtained in the pure condition after two crystallisations from dilute alcohol. It then melted at 135—136° and did not depress the melting point of an authentic specimen. A similar result was obtained when sulphuric acid (110 c.c.) was employed in

place of the hydrobromic acid. Since the melting-point test of identity is sometimes fallible, the nature of the product was further established by hydrolysing it (10 g.) by boiling for 4 hours with 50% sulphuric acid (although Noelting, Braun, and Thesmar, *loc. cit.*, p. 2260, state that they were unable to effect a satisfactory hydrolysis). The base (6·5 g.), b. p. 159—161°/24—25 mm., furnished a m-*nitrobenzoyl* derivative, which separated from alcohol in small rosettes, m. p. 170—171° (Found : N, 8·15. $C_{15}H_{13}O_3N_2Br$ requires N, 8·0%). Its melting point was depressed by addition of the isomeric compound described below.

(*d*) Bromination of *m*-2-xylidine in presence of glacial acetic acid was found by Noelting, Braun, and Thesmar to furnish the 5-bromo-derivative, but no yield was recorded. Repetition of their experiment gave the pure material in a yield of 88%, and no indication of the 4-isomeride was obtained on acetylation.

(*e*) Again, the addition of bromine (8 g.) to a solution of the base (6 g.) in hydrobromic acid (b. p. 126°; 40 c.c.) at 15—20° yielded the 5-bromo-derivative, together with some oily material (2·3 g.). This oil was recovered by extraction of the porous earthenware used to dry the crude product, and on acetylation it was found to consist essentially of the 5-bromo-base. This was further characterised by its m-*nitrobenzoyl* derivative, which separated from dilute acetic acid in long needles, m. p. 186—187° (Found : N, 8·2. $C_{15}H_{13}O_3N_2Br$ requires N, 8·0%).

Chlorination Experiments.—*4-Chloro-2-nitro*-m-*xylene*, prepared from 2-nitro-*m*-4-xylidine, separated from alcohol in yellow needles, m. p. 72—73° (Found : N, 7·9. $C_8H_8O_2NCl$ requires N, 7·5%). It was converted by means of tin and hydrochloric acid into 4-*chloro*-m-2-*xylidine*, b. p. 136—138°/17 mm. (Found : N, 9·1. $C_8H_{10}NCl$ requires N, 9·0%). 4-*Chloroaceto*-m-2-*xylidide* crystallises from dilute alcohol in white needles, m. p. 146—147° (Found : N, 7·2. $C_{10}H_{12}ONCl$ requires N, 7·1%).

5-*Chloro*-2-*nitro*-m-*xylene*, prepared from 2-nitro-*m*-5-xylidine, forms plates, m. p. 44—45° (Found : N, 7·75%). 5-*Chloro*-m-2-*xylidine* crystallises in long, silky needles, m. p. 44—45° (Found : N, 9·0%); it was characterised by its *acetyl* derivative, which separates from dilute alcohol in plates, m. p. 195° (Found : N, 7·0%).

A solution of *m*-2-xylidine (25 g.) in glacial acetic acid (150 c.c.) was treated at 10—15° with dry chlorine, generated from potassium permanganate (15 g.). After 2 hours, the dark blue mixture was diluted, rendered alkaline, and distilled in steam. The first portion of distillate was separated as likely to contain any unchlorinated material, and the oil in it did not solidify. Subsequent portions, however, solidified and furnished 5-chloro-*m*-2-xylidine (15 g.),

m. p. 42°, which was identified by direct comparison with authentic base. A considerable proportion of the material was not volatile in steam, and probably consisted of more highly chlorinated material. Similar results are well known to follow chlorination of the toluidines and their acetyl derivatives, and render chlorinations not very suitable for the present purpose. For the time, therefore, this method was not further pursued.

Nitration Experiments.—(*a*) m-*Nitrobenzo*-m-2-*xylidide*, prepared from *m*-2-xylidine and *m*-nitrobenzoyl chloride in presence of pyridine, separated from alcohol in needles, m. p. 188—189° (Found: N, 10·6. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). A mixture of nitric (*d* 1·42; 1·6 g.) and sulphuric (10 g.) acids was added at 0° to a solution of *m*-nitrobenzo-*m*-2-xylidide (6·5 g.) in sulphuric acid (20 g.). The product was isolated after 12 hours in small, yellow needles, m. p. 165—166° (5·5 g.) after crystallisation from alcohol. Its constitution was established both by its identity with authentic m-*nitrobenzo*-4-*nitro*-m-2-*xylidide*, m. p. 170·5°, prepared from 4-nitro-*m*-2-xylidine (Found: N, 13·5. $C_{15}H_{13}O_5N_3$ requires N, 13·3%), and by hydrolysis with 75% sulphuric acid to 4-nitro-*m*-2-xylidine, m. p. 81°.

(*b*) A similar result was obtained when the m-*nitrobenzoyl* derivative (3 g.) was dusted into nitric acid (*d* 1·42; 15 c.c.) at 25°, and the temperature finally allowed to rise to 50°.

Substitution in m-4-*Xylidine and its Derivatives.*

Bromination Experiments.—(*a*) The statement that aceto-*m*-4-xylidide undergoes bromination in the 6-position in glacial acetic acid solution (Genz, *loc. cit.*; Noelting, Braun, and Thesmar, *loc. cit.*) was confirmed.

(*b*) A mixture of bromine (4 g.) with aceto-*m*-4-xylidide (4 g.) and hydrobromic acid (b. p. 126°; 60 c.c.) was not decolorised even after 8 days. The product, after repeated crystallisation from dilute alcohol, yielded 6-bromoaceto-*m*-4-xylidide (1 g.), m. p. 168—169°, whilst by hydrolysis of the residues with 50% sulphuric acid 1 g. of the corresponding base, m. p. 96—97°, was recovered.

(*c*) The acetyl derivative (5 g.) was very slowly attacked at the ordinary temperature by bromine (5 g.) in chloroform solution (50 c.c.) in presence of iron wire. The product, isolated after 24 hours, yielded 1 g. of 6-bromo-*m*-4-xylidine, m. p. 96—97°. Another experiment showed that bromination was far from complete even after 6 weeks.

Nitration Experiments.—(*a*) m-*Nitrobenzo*-m-4-*xylidide* forms white needles, m. p. 162—163° (Found: N, 10·4. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). The compound (3 g.) was dusted into nitric

acid (*d* 1·42; 15 c.c.) at 5—10°, and the temperature was allowed to rise to 30°; the product, after crystallisation from glacial acetic acid, furnished 2·4 g. of material, m. p. 209—210°, identical with authentic m-*nitrobenzo*-5-*nitro*-m-4-*xylidide*, m. p. 210—211° (Found : N, 13·4. $C_{15}H_{13}O_5N_3$ requires N, 13·3%).

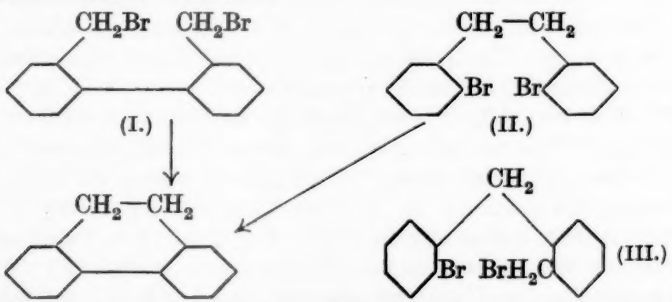
(*b*) Addition of a mixture of nitric acid (*d* 1·48; 1·6 g.) with sulphuric acid (10 g.) to a solution of *m*-nitrobenzo-*m*-4-xylidide (5 g.) in sulphuric acid (20 g.) at 0° furnished a product (5 g.), from which needles, m. p. 217—218°, were obtained by crystallisation from glacial acetic acid. The essential nature of the material followed from its identity with authentic m-*nitrobenzo*-6-*nitro*-m-4-*xylidide*, m. p. 224—225° (Found : N, 13·3%), and from its hydrolysis by alcoholic sodium hydroxide to 6-nitro-*m*-4-xylidine, m. p. 117—118°.

THE UNIVERSITY, SYDNEY. [*Received, March 9th*, 1927.]

CLI.—*Jackson and White's Synthesis of Phenanthrene.*

By JAMES KENNER and JOHN WILSON.

IT was shown some years ago (Kenner and Turner, J., 1911, **109**, 2101) that ωω′-dibromo-2 : 2′-ditolyl (I) is converted by treatment with sodium into a product from which, by oxidation, phenanthraquinone is obtained to the extent of 26% of that theoretically possible. At the same time it was pointed out that the initial material represents one of the possible intermediate products in the conversion of *o*-bromobenzyl bromide into a phenanthrene derivative through the agency of sodium.



The yield of phenanthraquinone obtained by Jackson and White (*Amer. Chem. J.*, 1880, **2**, 383) in this manner amounted, however, to only 2·66%. On the other hand, consideration of the relative reactivities of the two bromine atoms in *o*-bromobenzyl bromide

suggests 2 : 2′-dibromodibenzyl (II) as the compound most likely to be produced in the first stages of the reaction. Since, then, anthracene was isolated to the extent of nearly 20% of that theoretically possible, and presumably was derived from 2-bromophenyl-ω-bromo-*o*-tolylmethane (III), it appeared that the action of sodium on 2 : 2′-dibromodibenzyl must furnish as chief product some other compound than dihydrophenanthrene, and it became of interest to investigate this point experimentally.

The dibromo-compound was prepared by the reaction discovered by Busch and Weiss (*Ber.*, 1900, **33**, 2701), consisting in the oxidation of *as*-dibenzylhydrazines by mercuric oxide :

$$(CH_2Ph)_2N{\cdot}NH_2 + HgO = CH_2Ph{\cdot}CH_2Ph + N_2 + H_2O + Hg.$$

It was then found that 2 : 2′-*dibromodibenzyl* is converted by treatment with sodium to the extent of more than 50% into dibenzyl, accompanied by other products, including phenanthrene or its dihydro-derivative. By oxidation of the mixture, phenanthraquinone was obtained in a yield of 12% of that theoretically possible, calculated on the weight of the original material. Whilst, therefore, the earlier synthesis connected phenanthrene with ditolyl, the present work, like Pschorr's valuable general synthesis, shows its relationship to dibenzyl.

The formation of dibenzyl, which was also noted by Jackson and White in their experiments, represents a not uncommon type of side reaction in syntheses of this kind (compare Schlubach and Goes, *Ber.*, 1922, **55**, 2889) and is perhaps not surprising in this instance, since Ullmann (*Annalen*, 1904, **332**, 40) found that only a 5% yield of diphenyl is obtained from bromobenzene by the Fittig reaction. In dibromoditolyl, this stage of the synthesis is already achieved, so that a better yield of phenanthrene derivative is obtained from this compound.

By applying the above result to the data supplied by Jackson and White, it is possible to account for almost the whole of their material on the hypothesis that dibromodibenzyl is the source of the phenanthrene derivative obtained by them. Thus their yield of 2·66% involves conversion of 22·2% of the original material into dibromodibenzyl. Their observation that only 75·4% of the total available bromine was eliminated as sodium bromide would correspond to 49·2% of material of which debromination was only half complete. These amounts, together with 19·8% converted into anthracene and 12·5% into products of indeterminate character, account satisfactorily for all the material, and it may therefore be concluded that the phenanthrene derivative obtained by Jackson and White originated for the most part from dibromodibenzyl.

When the reaction between *o*-bromobenzyl bromide and hydrazine hydrate in alcoholic solution was carried out either at the ordinary temperature or at 100°, the desired product was accompanied by a considerable proportion of *tri*-o-*bromobenzylhydrazine*,

$$(C_6H_4Br\cdot CH_2)_2N\cdot NH\cdot CH_2\cdot C_6H_4Br \text{ (IV)},$$

and of non-basic material, corresponding in composition to o-*bromobenzylidenedi*-o-*bromobenzylhydrazone*,

$$(C_6H_4Br\cdot CH_2)_2N\cdot N{:}CH\cdot C_6H_4Br \text{ (V)}.$$

In their analogous preparation of dibenzylhydrazine, Busch and Weiss (*loc. cit.*) had similarly noted the formation of benzylidenebenzylhydrazone, and tentatively explained it by the equation :

$$2(CH_2Ph)_2N\cdot NH_2 = (CH_2Ph)_2N\cdot N{:}CHPh + CH_2Ph\cdot NH\cdot NH_2.$$

Although, in support of this view, they described the isolation of the hydrazone as a product of the reduction of dibenzylnitrosoamine, Busch and Weiss were unable to detect the benzylhydrazine formulated as the second product, and it will also be seen that the two sides of the equation do not balance. In our experiment, it seemed simpler to attribute the formation of (V) to oxidation of (IV), and in fact this reaction was shown to occur rapidly and quantitatively when the hydrochloride of (IV) was boiled in alcoholic solution with a little cupric oxide. Busch and Weiss observed the formation of tribenzylhydrazine in their experiment, whilst Franzen and Kraft (*J. pr. Chem.*, 1911, **84**, 157) showed that it could be obtained by direct benzylation of hydrazine, and also prepared it from benzylidenedibenzylhydrazone by reduction.

A further study of the reaction between benzyl chloride and hydrazine showed that some tribenzylhydrazine is produced even when the amount of hydrazine used is twice that required for dibenzylation, whilst when the reactants in equimolecular proportion were heated in alcoholic solution, the tribenzylhydrazine, which constituted the main product, was accompanied by some tetrabenzylhydrazine. This compound had previously been prepared by Wieland and Schomberg by treating tribenzylhydrazine with benzyl bromide (*Ber.*, 1920, **53**, 1329).

Finally, it was shown that tribenzylhydrazine hydrochloride could be oxidised to benzylidenedibenzylhydrazone by atmospheric oxygen in hot dilute alcoholic solution.

Experimental.

Comparative experiments showed decomposition of a solution of *o*-toluenediazonium bromide with Naturkupfer C, first at 0° and ultimately at 40°, to be the best method of preparing *o*-bromotoluene. Its monobromination was achieved very satisfactorily at 135° by

adding 75% of the calculated quantity of bromine. *o*-Bromobenzyl bromide, separated by fractionation, boiled at 129°/19 mm.

Interaction of o-*Bromobenzyl Bromide and Hydrazine.*—When a cooled solution of the bromide (10 g.) in alcohol (15 c.c.) was treated with hydrazine hydrate (2·5 g.), a vigorous reaction occurred with evolution of heat and separation of an oily layer of aqueous hydrazine hydrochloride. This salt separated in needles after the mixture had been boiled for 1 hour and concentrated to one-third of the original bulk and the residue cooled. The other products were isolated by extracting the supernatant liquor with ether, after dilution with water (1 l.). When the dried ethereal solution was treated with an alcoholic solution of hydrogen chloride, *di*-o-*bromobenzylhydrazine hydrochloride* (3·5 g.), m. p. 205°, was precipitated. After purification by solution in alcohol (35 c.c.) and precipitation by ether (70 c.c.), it was obtained in matted, colourless needles, m. p. 214° (Found : N, 7·1; equiv., 406. $C_{14}H_{14}N_2Br_2$,HC2 requires N, 6·9%; equiv., 406·5). Its *benzylidene* derivative forms white plates, m. p. 116° (Found : N, 6·2. $C_{21}H_{18}N_2Br_2$ requires N, 6·1%).

Tri-o-*bromobenzylhydrazine hydrochloride*, which crystallises in hexagonal prisms, m. p. 194° (Found : N, 4·9. $C_{24}H_{19}N_2Br_3$,HCl requires N, 4·9%), is soluble in a mixture of alcohol and ether. It separated from the mother-liquor after precipitation of dibromobenzylhydrazine hydrochloride in the manner just described. Both were, however, precipitated when dry hydrogen chloride was passed directly into the above dried ethereal solution. The tribromobenzyl derivative was rapidly oxidised in boiling alcoholic solution by cupric oxide, and gradually by atmospheric oxygen during recrystallisation, to o-*bromobenzylidenedi*-o-*bromobenzylhydrazine*, which formed prisms, m. p. 108° (Found : N, 5·4; Br, 44·9. $C_{21}H_{17}N_2Br_3$ requires N, 5·2; Br, 44·7%).

Synthesis of Phenanthraquinone.—*2 : 2′-Dibromodibenzyl* was obtained in almost quantitative yield by adding yellow mercuric oxide to a solution of dibromodibenzylhydrazine, prepared by shaking the hydrochloride with dilute sodium hydroxide solution and chloroform. It separated from alcohol in plates, m. p. 84·5° (Found : Br, 47·15. $C_{14}H_{12}Br_2$ requires Br, 47·1%).

When the dibromo-derivative (5 g.) was boiled under reflux with a suspension of sodium powder (5 g.) in dry ether for 14 days, 96·6% of the bromine was obtained in the ionic condition. On evaporation, the ethereal solution furnished an oil (2·60 g.), from which dibenzyl (1·42 g.) crystallised. This was purified by steam distillation and identified by comparison with an authentic specimen. In two concordant experiments, oxidation of the oil by a solution of chromic acid in glacial acetic acid, followed by the usual procedure for

purification, yielded phenanthraquinone corresponding to 12% of that theoretically possible.

Interaction of Benzyl Chloride with Hydrazine.—(a) The observation that dibromodibenzylhydrazine yields a monohydrochloride rendered it necessary to examine the product described by Busch and Weiss as the dihydrochloride of dibenzylhydrazine. Analysis showed the salt, m. p. 202° (Busch and Weiss give m. p. 200°), to be a *monohydrochloride* (Found: N, 11·5; equiv., 249·5. $C_{14}H_{16}N_2,HCl$ requires N, 11·3%; equiv., 248·5).

(b) In order to study its tendency to oxidise, tribenzylhydrazine was prepared by boiling benzyl chloride (22 g.), hydrazine hydrate (8·7 g.), and alcohol (25 c.c.) together for 1 hour and finally concentrating the mixture to one-third of its original bulk. Hydrazine hydrochloride separated on cooling; the filtrate was then diluted and extracted with ether. From the dried ethereal solution tribenzylhydrazine hydrochloride (22 g.), m. p. 181° (Found: N, 4·9%; equiv., 336), was obtained by treatment with alcoholic hydrogen chloride. Tetrabenzylhydrazine, m. p. 139° (Found: N, 7·3%), was isolated in small amount from the liquor.

When air was passed through a boiling solution of tribenzylhydrazine hydrochloride (1 g.) in alcohol (100 c.c.) for 8 hours, 0·25 g. of pure benzylidenedibenzylhydrazine, m. p. 87°, was obtained, whereas a quantitative yield was obtained after a few minutes in presence of cupric oxide. Dibenzylhydrazine hydrochloride, on the other hand, did not undergo atmospheric oxidation.

A series of experiments in which benzyl chloride was similarly treated with variously excessive proportions of hydrazine hydrate showed that the formation of tribenzylhydrazine and the corresponding hydrazone to a greater or less extent always accompanies that of dibenzylhydrazine. The formation of the hydrazone observed by Busch and Weiss may therefore safely be ascribed to oxidation of tribenzylhydrazine. Separation of the two hydrazine hydrochlorides was effected by taking advantage of the smaller solubility of the dibenzyl derivative in ether and by crystallising the tribenzyl derivative from alcohol.

This work was carried out during the tenure by one of us (J. W.) of a Town Trustee Fellowship at the University of Sheffield.

THE UNIVERSITY, SHEFFIELD. [*Received, March 9th*, 1927.]

CLII.—*Piperidine as a General Reagent for the Determination of the Constitution of Halogenonitrocompounds. The Nitration of* 4 : 4′*-Dihalogenodiphenylmethane and* -s*-diphenylethane.*

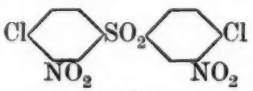
By Raymond James Wood Le Fèvre and Eustace Ebenezer Turner.

In this paper are described a number of piperidino-compounds the preparations and properties of which have led us to the conclusion that, as a reagent for reactive halogen atoms, piperidine is superior to alcoholic ammonia, aromatic amines, alkali alkyloxides, etc. The advantages contributing to this superiority include the following: (1) The substituted phenylpiperidines produced are as a rule highly crystalline. (2) Piperidine appears to react much more readily than most bases with mobile halogen atoms. (3) The interaction of piperidine and halogeno-compounds is generally characterised by the absence of by-products, whereas with hydrazines and alkali alkyloxides, for example, a mixture of products is usually obtained (compare Brand, *J. pr. Chem.*, 1903, **67**, 145; Lobry de Bruyn, *Rec. trav. chim.*, 1890, **9**, 203).

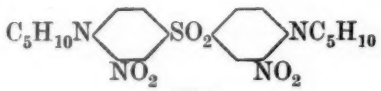
A few isolated piperidine compounds have been described in the past, notably by Lellmann and by Borsche. Lellmann was, however, not concerned with piperidine as a reagent, and Borsche, in employing piperidine, uses a method which in our hands has given most unsatisfactory yields (see Experimental).

Some examples follow illustrating the use of piperidine as a general reagent for reactive halogen atoms present in a number of compounds of known constitution.

The constitution (I) of the product of nitrating 4 : 4′-dichlorodiphenylsulphone was established by Ullmann and Korselt (*Ber.*, 1907, **40**, 643), using aniline and ammonia as reagents for reactive chlorine. Piperidine readily converts (I) into 3 : 3′*-dinitro*-4 : 4′*-dipiperidinodiphenylsulphone* (II).



(I.)



(II.)

Similarly, 2 : 5-dibromonitrobenzene is converted by piperidine into 4*-bromo*-2*-nitropiperidinobenzene*. In the case of 2 : 4-dichloronitrobenzene both halogens rapidly react with piperidine to give 1*-nitro*-2 : 4*-dipiperidinobenzene*.

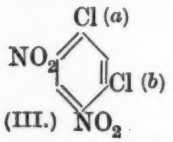
3 : 4-Dichloronitrobenzene would be expected to react once only

with piperidine and does so to give 2-*chloro*-4-*nitropiperidinobenzene*. 2 : 4 : 5-Trichloronitrobenzene, however, gives 4 : 5-*dichloro*-1-*nitro*-2-*piperidinobenzene* and not 5-chloro-1-nitro-2 : 4-dipiperidinobenzene, a fact which may be attributed to the combined steric and deactivating effects of the 5- on the 4-chlorine atom. The constitution of the product is proved below.

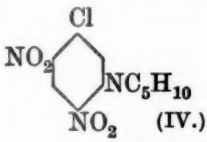
On the other hand, the introduction of a third group, *e.g.*, carboxyl or carbethoxyl, which by itself has feeble activating effect, produces a very marked exaltation of reactivity when its effect supports that of the nitro-group. Thus, towards piperidine, ethyl 2-chloro-5-nitrobenzoate, 4-chloro-3-nitrobenzoic acid, and 2 : 4-dichloronitrobenzene react apparently with the same vigour as does 1-chloro-2 : 4-dinitrobenzene.

The binuclear halogenonitro-compounds mentioned in this paper are all further examples of the same fact, *i.e.*, they react much more rapidly and completely than does either *o*- or *p*-chloronitrobenzene. Similarly, Borsche and Exss (*Ber.*, 1923, **46**, 2353) obtained quantitative results showing that 4-chloro-3-nitroazobenzene was intermediate between 1-chloro-2-nitro- and 1-chloro-2 : 4-dinitro-benzene in degree of reactivity.

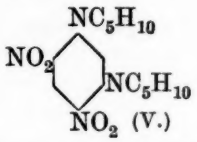
The investigation of 1 : 3-dichloro-4 : 6-dinitrobenzene by previous workers has already raised many interesting points. Thus, Borsche and Bahr (*Annalen*, 1913, **402**, 81) considered that in this compound (III) one chlorine atom (*a*) is less reactive than the other (*b*).



(III.)



(IV.)



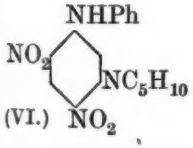
(V.)

The evidence for this assertion, apart from a very general reference to the work of "Nietzki and others" on the interaction of amines with this compound, consisted in the facts that ethyl sodio-malonate and -acetoacetate each reacted with only one chlorine atom, and that a second similar group was introduced only with difficulty. In the same paper there is described the compound (IV), and we therefore expected to find that the dichlorodinitrobenzene would, even under conditions sufficing to effect the conversion, *e.g.*, of 2 : 4-dichloronitrobenzene into 1-nitro-2 : 4-dipiperidinobenzene, give mainly (IV) and that the corresponding *dipiperidino*-compound (V) would be obtainable only with difficulty. Actually the reverse was the case. Borsche and Bahr's compound (IV) was certainly obtainable if care were exercised, but in presence of a slight excess of piperidine there occurred rapid formation of (V), which is very

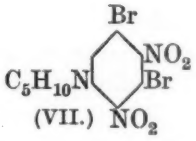
readily obtainable by warming the dichlorodinitrobenzene with enough piperidine to dissolve it. Moreover, the chlorine atom in (IV) is sufficiently mobile to react rapidly with aniline to give 4 : 6-*dinitro*-3-*anilino*-1-*piperidinobenzene* (VI).

Kenner (J., 1914, **105**, 2717) and Davies and Hickox (J., 1922, **121**, 2640) also have criticised some of Borsche's conclusions in connexion with other work on 1 : 3-dichloro-4 : 6-dinitrobenzene. Similarly, we are unable to agree with Hodgson (*J. Soc. Dyers and Col.*, 1926, 42) that the existence of two forms of 1-chloro-3-bromo-4 : 6-dinitrobenzene is capable of satisfactory explanation only by means of Borsche's conceptions, since at least six halogenonitrobenzenes, including 1 : 3-dibromo-4 : 6-dinitrobenzene (Jackson and Cohol, *Amer. Chem. J.*, 1903, **26**, 4), have been found to exhibit polymorphism.

1 : 3 : 5-Tribromo-2 : 4-dinitrobenzene is readily converted by two mols. of piperidine into a compound which we regard as 1 : 3-*dibromo*-2 : 4-*dinitro*-5-*piperidinobenzene* (VII), since (Borsche and Rantscheff, *Annalen*, 1911, **379**, 152) the halogen atom in 2-chloro-1 : 3-dinitrobenzene is less reactive than that in 1-chloro-2 : 4-dinitrobenzene. Excess of piperidine converts the original tribromo-compound with violence into 2 : 4-dinitro-1 : 3 : 5-tripiperidinobenzene (VIII), a compound obtained by Borsche and Trautner (*Annalen*, 1926, **447**, 1) from 1 : 3 : 5-trichloro-2 : 4-dinitrobenzene. These authors report the m. p. as 147—148°, but it actually melts 30° higher, and it is possible that this affords another illustration of the unsatisfactory nature of Borsche's method of using piperidine (see Experimental).



(VI.)



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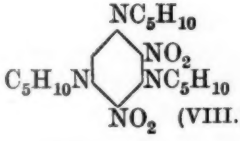
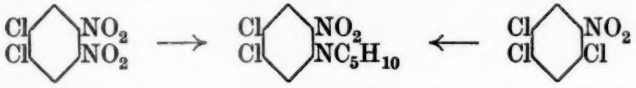


(VIII.)

The possibility of a reaction occurring owing to the activating effect of an ortho-para- on a meta-orienting substituent in the *m*-position to it, which has been observed in a few instances, *e.g.*, Tiemann (*Ber.*, 1891, **24**, 709), Kenner and others (J., since 1914), and Morgan (J., 1920, **117**, 784; 1921, **119**, 1537), has not been overlooked. It seems, however, that when there is no great crowding of groups, particularly nitro-groups, evidence based on the removal of halogen is trustworthy, *i.e.*, in general, only that halogen is labile which is in the *o*- or *p*-position to the nitro-group.

A reaction of piperidine with a compound having a labile nitro-

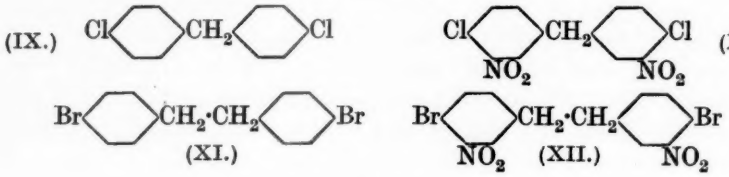
group has been utilised to prove the constitution of the product obtained from 2 : 4 : 5-trichloro-1-nitrobenzene and piperidine.



Thus, 1 : 2-dichloro-4 : 5-dinitrobenzene reacts readily with piperidine to give 4 : 5-dichloro-2-nitropiperidinobenzene, a nitro-group being replaced by a piperidino-group.

4 : 4′-Dichlorodiphenylmethane (IX) on nitration gave mainly 4 : 4′-*dichloro*-3 : 3′-*dinitrodiphenylmethane* (X), the constitution of which follows from its conversion, by piperidine, into 3 : 3′-*dinitro*-4 : 4′-*dipiperidinodiphenylmethane*.

The nitration of 4 : 4′-dibromo-*s*-diphenylethane (XI) was far from quantitative, but a nitro-derivative was isolated with a m. p. ascribed in the literature to 4 : 4′-dibromo- ? : ?-dinitro-*s*-diphenylethane, and therefore evidently the main, or most readily isolable, product of the nitration. Since piperidine converted this compound into a *dipiperidino*-compound, it is clearly 4 : 4′-*dibromo*-3 : 3′-*dinitro*-s-*diphenylethane* (XII).



EXPERIMENTAL.

General Method of Preparation of Piperidino-derivatives.—Except where otherwise stated, these derivatives were prepared by gently boiling, for 3 minutes, the halogenonitro-compound with that amount of piperidine which effects complete solution. In cases where interaction was violent, a solvent such as alcohol was also used. As a rule, reaction was accompanied by the appearance of a bright red colour, the cooled product usually setting to a crystalline magma of piperidine hydrohalide. Water was added, and frequently solidification then ensued. Two methods of inducing crystallisation were particularly effective in cases of delayed solidification due to the presence of a trace of water or of unchanged halogen-compound: (*a*) The oily piperidino-derivative was dissolved in benzene, and the solution left over anhydrous sodium sulphate for a few minutes. Evaporation of the filtered solvent followed by desiccation in a vacuum, in most cases caused solidification. (*b*) In other cases, the oily derivative was warmed with dilute mineral

acid, and the liquid was cooled, filtered, and basified. These two methods are referred to below as treatments (*a*) and (*b*) respectively.

3 : 3′-*Dinitro*-4 : 4′-*dipiperidinodiphenylsulphone* (II).—4 : 4′-Dichloro-3 : 3′-dinitrodiphenylsulphone gave a yellow coloration with cold piperidine and reacted violently with the latter on warming. The crude product was solid, was only slightly soluble in carbon tetrachloride, chloroform, benzene, or toluene, but was more soluble in acetone and methyl alcohol. It separated from methylated spirit in long, yellow needles, m. p. 183·5° (Found : N, 11·9. $C_{22}H_{26}O_6N_4S$ requires N, 11·8%).

4-*Bromo*-2-*nitropiperidinobenzene*.—The oily product of the interaction of 2 : 5-dibromonitrobenzene did not solidify after treatment (*a*), but did so after treatment (*b*). It separated from alcohol in deep red prisms, m. p. 48—49° (Found : Br, 28·1. $C_{11}H_{13}O_2N_2Br$ requires Br, 28·1%).

1-*Nitro*-2 : 4-*dipiperidinobenzene*.—The product of interaction of 2 : 4-dichloronitrobenzene and piperidine solidified after treatment (*a*). The crude piperidino-derivative was a mass of red-orange needles, m. p. 63—64°. When the solution in alcohol was cooled, there was a sudden deposition of radiating bunches of hexagonal leaflets, m. p. 67—68° (Found : N, 14·8. $C_{16}H_{23}O_2N_3$ requires N, 14·5%).

2-*Chloro*-4-*nitropiperidinobenzene*.—3 : 4-Dichloronitrobenzene and piperidine gave a yellow solution in the cold, and reacted vigorously on warming. Treatment (*b*) was necessary to induce solidification and then crystallisation from aqueous alcohol gave small, lemon-yellow plates, m. p. 47—48° (Found : N, 12·4; Cl, 14·9. $C_{11}H_{13}O_2N_2Cl$ requires N, 11·6; Cl, 14·8%).

4 : 5-*Dichloro*-1-*nitro*-2-*piperidinobenzene*.—2 : 4 : 5-Trichloronitrobenzene reacted with piperidine to give an oil which solidified only after treatment (*a*). It then separated from alcohol in red prisms, m. p. 64—65° (Found : Cl, 25·9. $C_{11}H_{12}O_2N_2Cl_2$ requires Cl, 25·8%).

5-*Nitro*-2-*piperidinobenzoic Acid and the Corresponding Ethyl Ester*.—*o*-Chlorobenzoic acid (55 g.) was added to 300 g. of nitric acid (*d* 1·5), and the resulting solution, after being left for 10 minutes, was poured on ice. The crude nitro-acid (42·5 g.) melted at 163—164°, whereas Hübner, for the pure acid, gives 165° (*Annalen*, 1884, 222, 195).

The 2-chloro-5-nitrobenzoic acid reacted readily with piperidine to give the *piperidino-acid*, m. p. 201—202°, and when heated with alcohol and concentrated sulphuric acid gave the ethyl ester as a pale yellow oil, b. p. 190—191°/16 mm., solidifying at about 25°. Ethyl 2-chloro-5-nitrobenzoate reacted vigorously with piperidine without the application of heat. Treatment (*a*) led to the solidi-

fication of *ethyl 5-nitro-2-piperidinobenzoate*, which separated from aqueous alcohol in bright yellow, rectangular plates, m. p. 78—79° (Found: N, 10·2. $C_{14}H_{18}O_4N_2$ requires N, 10·1%).

3-Nitro-4-piperidinobenzoic Acid.—Addition of the diazo-solution prepared from *p*-chloroaniline (hydrochloric acid) to a solution of potassium cuprocyanide gave a 45% yield of almost pure *p*-chlorobenzonitrile. Nitration of the latter with nitric acid (*d* 1·5) at 5° gave a crude 4-chloro-3-nitrobenzonitrile, m. p. about 94°. Crystallisation from alcohol gave a product melting at 100—101°, as recorded by Claus and Kurz (*J. pr. Chem.*, 1888, **37**, 197), who obtained the nitrile from 4-chloro-3-nitroaniline by the diazo-process.

The nitrile was converted by piperidine into 3-nitro-4-piperidinobenzonitrile, m. p. 110—111° (compare Borsche, Stackmann, and Makaroff-Semljanski, *Ber.*, 1916, **49**, 2222), and by boiling 70% sulphuric acid into 4-chloro-3-nitrobenzoic acid. The latter reacted with piperidine quite as readily as did 2-chloro-5-nitrobenzoic acid, and the product (m. p. 202—203°) was evidently identical with that obtained by the last-mentioned authors by hydrolysing 3-nitro-4-piperidinobenzonitrile, the latter being obtained by them from 4-bromo-3-nitrobenzonitrile and piperidine.

Ethyl 3-nitro-4-piperidinobenzoate was obtained by esterification of the corresponding acid, with alcohol and sulphuric acid, as a red, viscous syrup (Found: N, 10·0. $C_{14}H_{18}O_4N_2$ requires N, 10·1%).

Behaviour of Piperidine towards o-Chlorobenzoic Acid.—(*a*) The acid was recovered unchanged after being heated for 6 hours with piperidine at the b. p. of the mixture. (*b*) The acid was heated with anhydrous potassium carbonate and piperidine in the presence of a little copper bronze. It was converted into salicylic acid.

4 : 6-Dinitro-1 : 3-dipiperidinobenzene (V).—Since 1 : 3-dichloro-4 : 6-dinitrobenzene reacted explosively in the cold, it was dissolved in pyridine and excess of piperidine added slowly, with external cooling. The dark brown, crystalline paste was filtered off; the solid so obtained separated from glacial acetic acid in dark yellow leaflets, m. p. 130—131° (Found: N, 16·9. $C_{16}H_{22}O_4N_4$ requires N, 16·8%).

3-Chloro-4 : 6-dinitropiperidinobenzene (IV).—A solution of 3·6 g. of piperidine in 15 c.c. of alcohol was added, slowly and with shaking, to a solution of 4 g. of 1 : 3-dichloro-4 : 6-dinitrobenzene in 50 c.c. of alcohol. The mixture was gently boiled for 10 minutes and then diluted with water, and the resulting yellow product was washed and crystallised thrice from alcohol. It then had m. p. 119° (compare Borsche and Bahr, *loc. cit.*).

4 : 6-Dinitro-3-anilino-1-piperidinobenzene (VI).—The previous

compound was heated with excess of aniline for 3 minutes, and the cooled solution was then poured into excess of dilute hydrochloric acid. The resulting black, brittle, solid product, after two crystallisations from glacial acetic acid, formed bright yellowish-green plates, m. p. 148—148·5° (Found: N, 16·6. $C_{17}H_{18}O_4N_4$ requires N, 16·4%).

Action of Piperidine on 1 : 3 : 5-*Tribromo*-2 : 4-*dinitrobenzene.*—(*a*) To a solution of 4 g. (1 mol.) of tribromodinitrobenzene in 25 c.c. of boiling chloroform were added 2·2 c.c. (2·25 mols.) of piperidine dissolved in 10 c.c. of chloroform. The solution was then boiled for a further 2 minutes, the chloroform removed by evaporation, and the residue extracted with water. The residue, on crystallisation from alcohol, gave 1 : 3-*dibromo*-2 : 4-*dinitro*-5-*piperidinobenzene* (VII) in yellow plates, m. p. 125—126° (Found: Br, 39·0. $C_{11}H_{11}O_4N_3Br_2$ requires Br, 39·1%).

(*b*) With 4·3 c.c. of piperidine and 4 g. of the tribromo-compound, under the above conditions, a mixture was obtained.

(*c*) When the tribromo-compound was treated with excess of piperidine a violent reaction at once set in, and even with careful cooling it was found difficult to prevent some *actual charring* in the centres of the masses formed. Addition of water, filtration, and crystallisation from alcohol led to yellow needles of 2 : 4-dinitro-1 : 3 : 5-tripiperidinobenzene (VIII), m. p. 177—178° (Found: N, 16·5. $C_{21}H_{31}O_4N_5$ requires N, 16·8%).

1 : 2-*Dichloro*-4 : 5-*dinitrobenzene.*—The preparation of this substance from *o*-dichlorobenzene by the method described by Hartley and Cohen (J., 1904, **85**, 867) is very tedious, since even after two lengthy nitration processes the product is a mixture. We have found it more convenient to nitrate *o*-dichlorobenzene, separate the 3 : 4-isomeride—a comparatively simple matter—and nitrate it. 3 : 4-Dichloronitrobenzene (10 g.) was dissolved in 60 c.c. of nitric acid (*d* 1·5), and 40 c.c. of fuming sulphuric acid (20% SO_3) were added. The solution was heated for 2 hours at 100°, then cooled and poured into water. The solid precipitated, after being twice crystallised from dilute acetic acid, gave the dinitro-compound, m. p. 109—110° (Hartley and Cohen give 104°; Nietzki and Konwaldt, *Ber.*, 1904, **37**, 3892, give 114°).

Action of Piperidine on 1 : 2-*Dichloro*-4 : 5-*dinitrobenzene.*—This chloronitro-compound reacted in the cold with piperidine. The reaction was completed by boiling for a few minutes, and the resulting solution was treated with water. The red oil precipitated was washed with very dilute hydrochloric acid and then with water. Crystals, m. p. 62—64°, separated on inoculation of an alcoholic solution with solid obtained as above from trichloronitrobenzene.

The two products were identical. The unidirectional nature of the reaction just described is perhaps worth comment. Aniline and other primary bases give products which are much less easily isolated.

4 : 4′-*Dichlorodiphenylmethane*.—Montagne (*Rec. trav. chim.*, 1906, **25**, 390, 412) had previously obtained this substance by reducing 4 : 4′-dichlorobenzophenone, but we have obtained it more conveniently as follows: 4 : 4′-Diaminodiphenylmethane (25 g.) was dissolved in 150 c.c. of concentrated hydrochloric acid with the addition of 150 c.c. of water. The suspension (obtained on cooling) was diazotised with 17 g. of sodium nitrite dissolved in 40 c.c. of water, ice being added at intervals to keep the temperature at 0°. The resulting clear solution (about 600 c.c.) was poured into a cooled solution of cuprous chloride in hydrochloric acid (made from 150 g. of copper sulphate pentahydrate). A biscuit-coloured copper compound separated, which decomposed when the mixture was warmed at 100° for 0·5 hour. The brown oil formed was extracted with benzene, and isolated by distillation under reduced pressure; 15 g. of dichloro-compound, b. p. 186—190°/18 mm., m. p. 55—56° (after one crystallisation from alcohol), were then obtained.

4 : 4′-*Dichloro*-3 : 3′-*dinitrodiphenylmethane* (X).—The dichloro-compound was added to eight times its weight of water-cooled nitric acid (*d* 1·5). After a few minutes, when crystals began to separate, the mixture was poured into excess of water. The precipitated solid was slightly soluble in light petroleum (b. p. 80—100°) and in acetone, but more soluble in benzene, chloroform, and alcohol. It separated from glacial acetic acid in white plates, m. p. 198—199° (Found: Cl, 21·6. $C_{13}H_8O_4N_2Cl_2$ requires Cl, 21·7%).

The dinitro-compound reacted normally with piperidine to give 3 : 3′-*dinitro*-4 : 4′-*dipiperidinodiphenylmethane*, which, after being crystallised first from glacial acetic acid and then from alcohol, melted at 183—184° (Found: N, 13·4. $C_{23}H_{28}O_4N_4$ requires N, 13·2%).

4 : 4′-*Dibromo*-3 : 3′-*dinitro*-s-*diphenylethane* (XII).—4 : 4′-Dibromo-*s*-diphenylethane, m. p. 114°, prepared by the direct bromination of *s*-diphenylethane (compare Stelling and Fittig, *Annalen*, 1866, **137**, 267) was added to 15 parts of water-cooled nitric acid (*d* 1·5). The solution was warmed gently for 15 minutes, cooled, and poured into water. The resulting gummy precipitate, when dry, separated from benzene with m. p. 155—160°. Two further crystallisations gave small, yellowish-white crystals, m. p. 204°, the figure given by Stelling and Fittig.

The dinitro-compound was converted by piperidine into a product which separated from glacial acetic acid in orange-yellow, microscopic needles, m. p. 235—240°, with previous shrinking (Found: N, 13·0. $C_{21}H_{30}O_4N_4$ requires N, 12·8%).

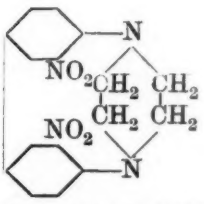
The Use of Sodium Acetate in the Preparation of Piperidino-compounds.—Borsche and his co-workers (*loc. cit.*) prepared a number of piperidino-compounds by heating 1 mol. of halogenonitro-compound with 1 mol. of piperidine hydrochloride (per 1 atom of reactive halogen) and excess of sodium acetate in alcoholic solution. Using this method with *p*-chloronitrobenzene, only a 36% yield has been obtained by us, whereas with 2·5 mols. of piperidine at 100°, almost theoretical conversion is effected.

Again, 4-chloro-3-nitrobenzonitrile gave only a 40% yield of piperidino-compound by Borsche's method, whilst almost theoretical yields were obtained by using piperidine alone at 100°.

1 : 4-*Di*-op-*dinitrophenylpiperazine.*—Piperazine (1 mol. of the hexahydrate) was heated with 3 mols. of 1-chloro-2 : 4-dinitrobenzene. At the b. p. of the mixture, sudden interaction occurred, and the previous two layers became an orange paste. After extraction with boiling alcohol and hot water, a product remained which was sparingly soluble in hot or cold glacial acetic acid, pyridine, acetone, or chloroform. It separated from nitrobenzene in orange-red needles, decomp. with effervescence at about 240° (Found : N, 20·3. $C_{16}H_{14}O_8N_6$ requires N, 20·1%).

1 : 4-*Di*-oop-*trinitrophenylpiperazine* (1 : 4-*dipicrylpiperazine*), prepared similarly, crystallised from nitrobenzene in orange needles, not melting at 260° (Found : N, 22·2. $C_{16}H_{12}O_{12}N_8$ requires N, 22·0%).

Interaction of Piperazine with 4 : 4′-*Dibromo*-3 : 3′-*dinitrodiphenyl.*—These two substances might conceivably interact to give a compound of the following structure (see, however, Le Fèvre and Turner, J., 1926, 2476) :



A solution of 1 g. of dibromodinitrodiphenyl and 0·5 g. of piperazine hexahydrate in 30 c.c. of pyridine was boiled for 2 hours, and then evaporated to a small bulk. The reddish-orange *powder* which separated on cooling, after crystallisation from pyridine, melted at about 215° (Found : N, 14·0. $C_{16}H_{15}O_4N_4Br$ requires N, 13·8%).

The substitution of benzidine for piperazine in the last experiment gave brown *needles*, from pyridine, m. p. 251° (Found : N, 10·8. $C_{24}H_{17}O_4N_4Br$ requires N, 11·1%).

In neither case, therefore, is a " Kaufler " compound formed.

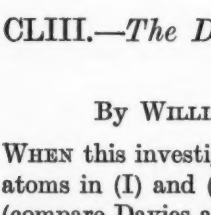
One of us (R. J. W. Le F.) has pleasure in acknowledging a maintenance grant from the Department of Scientific and Industrial Research, and also a grant allocated to him by the Research Grant Committee of the Chemical Society.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, March 12th*, 1927.]

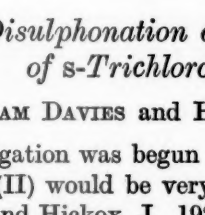
CLIII.—*The Disulphonation of* m-*Dichlorobenzene and of* s-*Trichlorobenzene.*

By WILLIAM DAVIES and HARRY GORDON POOLE.

WHEN this investigation was begun it was hoped that the chlorine atoms in (I) and (II) would be very reactive, as they are in (III) (compare Davies and Hickox, J., 1922, **121**, 2640), and would lend themselves to similar condensations. The easy elimination of the sulphonic groups from the condensation products would then give mixed aromatic–aliphatic compounds of some synthetic importance. The chlorine atoms in (I) and (II) are, however, practically non-reactive compared with those in (III), and the contemplated condensations could not be brought about.



(I.)



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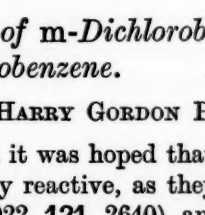

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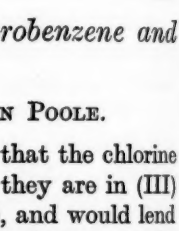


(IV.)

The disulphonic acid formed by the direct sulphonation of *m*-dichlorobenzene gives a sulphonyl chloride identical with that already prepared by the action of phosphorus pentachloride on salts of (IV) (Pollak and Wienerberger, *Monatsh.*, 1914, **35**, 1472). Hence the constitution (I) is justified. Nothing was previously known of the disulphonic acid of *s*-trichlorobenzene, which must, however, have the formula indicated (II). Both *m*-dichlorobenzene and *s*-trichlorobenzene are much less readily sulphonated than the corresponding methyl derivatives of benzene, despite the fact that the chlorine atom is considered to have a greater directive power than the methyl group (Holleman, *Chem. Reviews*, 1924—1925, I, 2, 202).

EXPERIMENTAL.

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonic Acid.*—*m*-Dichlorobenzene (30 g.) is dropped with cooling into fuming sulphuric acid (70 c.c.; 45% SO_3), and the mixture heated at 140—150° for 5 hours. The product after cooling and treatment with ice is converted into the

barium salt, and this into the sulphonyl chloride by heating it with phosphorus pentachloride at 130—140° for 6 hours. The sulphonyl chloride crystallises from petroleum (b. p. 100—120°) in large, thick rhombohedra, and also less frequently in long, thin needles, both forms melting at 122—123° (Pollak and Wienerberger, *loc. cit.*, record m. p. 122—123°). The crystals provide an excellent example of triboluminescence, the flashes being sufficiently brilliant to be seen in ordinary electric light (Found: C, 20·7; H, 0·9. Calc.: C, 20·9; H, 0·6%).

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonic acid* forms plates very soluble in water, and can be crystallised from concentrated sulphuric acid. The *amide*, colourless needles, m. p. 276°, is readily soluble in hot and sparingly soluble in cold water. The sodium and the barium salt are very soluble in cold water, but the *potassium* salt is very soluble in hot and only moderately easily soluble in cold water, from which it separates in colourless prisms (Found in the air-dried salt: H_2O, 1·25. $C_6H_2O_6Cl_2S_2K_2,\frac{1}{4}H_2O$ requires H_2O, 1·2. Found in anhydrous salt: K, 20·3. $C_6H_2O_6Cl_2S_2K_2$ requires K, 20·4%). When the potassium salt is boiled for 24 hours with excess of aqueous-alcoholic potassium hydroxide, the quantity of chlorine displaced is less than 0·5% of that calculated for the displacement of one atom of chlorine. Bromine water attacks the salts or the acid extremely slowly, in marked contrast to the action with *m*-xylene-4 : 6-disulphonic acid.

s-Trichlorobenzenedisulphonic Acid.—2 : 4 : 6-Trichloroaniline has hitherto been prepared by passing chlorine into a solution of aniline in chloroform (Meyer and Sudborough, *Ber.*, 1894, **27**, 3151; Willgerodt and Wilcke, *Ber.*, 1910, **43**, 2747). This process produces large quantities of mono- and di-chloroanilines, the formation of which is hindered in the following method. Aniline (100 g.) is added drop by drop to a cold solution of chlorine (160 g.) in carbon tetrachloride (1000 g.). During the reaction a good stream of chlorine is passed, and excess of chlorine maintained. It is essential to keep the reaction mixture cold during the experiment, which requires about 5 hours. The product is worked up after the method of Willgerodt and Wilcke (*loc. cit.*); the yield of trichloroaniline is 120 g. (W. and W. obtained 78 g.). The conversion of trichloroaniline into *s*-trichlorobenzene by the method of Jackson and Lamar (*J. Amer. Chem. Soc.*, 1896, **18**, 667) gives an excellent yield. The yield is increased by treating the residue with 70% sulphuric acid, in the usual way, to remove aniline.

s-Trichlorobenzene is recovered unchanged after being heated with concentrated sulphuric acid at 100° for 56 hours, and is only partly sulphonated when heated at this temperature with fuming

sulphuric acid (12% SO_3) for 6 hours. But when *s*-trichlorobenzene (9 g.) is heated on the water-bath with fuming sulphuric acid (25 c.c.; 72% SO_3) for 15 hours, complete disulphonation occurs. Disulphonation also takes place with this strength of acid in 5 hours at 115—120°, but the product is not so pure as that obtained at the lower temperature. The dry sodium salt (17 g.) is prepared *via* the calcium or barium sulphonate in the usual way, and when heated for 3 hours with three times its weight of phosphorus pentachloride and a little phosphorus oxychloride, is smoothly converted into the sulphonyl chloride (70% yield of the pure product). *s-Trichlorobenzenedisulphonyl chloride* crystallises from petroleum (b. p. 100—120°) or ethyl acetate in prisms, m. p. 161·5° (Found: Cl, 47·1; S, 16·6. $C_6HO_4Cl_5S_2$ requires Cl, 46·8; S, 16·9%). Owing to the high melting point of the sulphonyl chloride the *amide* cannot be easily obtained by the action of aqueous ammonia in the usual way; it is formed, however, by the addition of concentrated aqueous ammonia to the sulphonyl chloride in benzene. It is readily soluble in boiling and sparingly soluble in cold water, from which it separates in minute, colourless needles, m. p. 248° (Found: N, 8·5. $C_6H_5O_4N_2Cl_3S_2$ requires N, 8·3%).

s-Trichlorobenzenedisulphonic acid separates from concentrated sulphuric acid, in which it is moderately easily soluble, in colourless needles very soluble in water. The normal *sodium* salt is extremely soluble in water, and the normal *barium* salt (needles) dissolves in about its own weight of water at the ordinary temperature, but both salts are sparingly soluble in absolute alcohol. The *potassium* salt is slightly soluble in boiling and sparingly soluble in cold water, from which it crystallises in small, compact prisms (Found in air-dried material: H_2O, 0·1%. Found in anhydrous salt: K, 18·6. $C_6HO_6Cl_3S_2K_2$ requires K, 18·7%). Prolonged treatment of the potassium salt with boiling potassium hydroxide solution produces only a trace of potassium chloride, showing that the chlorine atoms are not reactive under the particular conditions investigated.

MELBOURNE UNIVERSITY. [*Received, March 15th*, 1927.]

CLIV.—*Some Experiments with* 1 : 8-*Naphthalyl Chloride.*

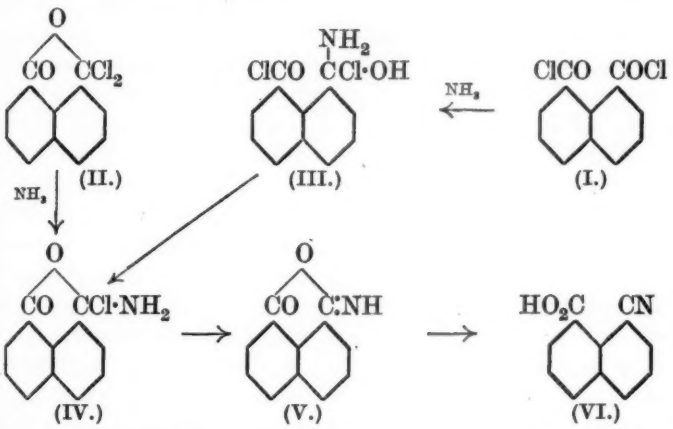
By WILLIAM DAVIES and GEOFFREY WINTHROP LEEPER.

IT is known that the dichlorides of several dicarboxylic acids (*e.g.*, *o*-phthalic acid) can exist in two tautomeric forms and it was therefore decided to examine 1 : 8-naphthalyl chloride (Mason, J., 1924,

125, 2116) in order to determine whether an analogous type of tautomerism could occur in this case; the examination, however, has failed to reveal the existence of more than one form, both distillation under 0·2 mm. pressure and treatment with aluminium chloride leaving the chloride unchanged.

Catalytic reduction of the chloride by Rosenmund's method (*Ber.*, 1921, **54**, 432) under conditions which gave an excellent yield of benzaldehyde from benzoyl chloride gave a complex mixture from which only naphthalic anhydride could be isolated.

The interactions of naphthalyl chloride and of phthalyl chloride with ammonia follow similar courses, but the production of 1-cyano-8-naphthoic acid can be explained equally well by either of the possible formulæ for naphthalyl chloride (I) or (II) *via* the inter-



mediate compounds (III), (IV), and (V) (compare Staudinger, *Ber.*, 1911, **44**, 1643). It is noteworthy, however, that ammonia reacts very slowly with the chloride in benzene solution.

The action of aniline and of dimethylaniline on naphthalyl chloride followed normal lines, yielding, respectively, 1 : 8-naphthaldianilide and 1 : 8-naphthalbisdimethylanilide.

The evidence obtained therefore leaves the question of the constitution of 1 : 8-naphthalyl chloride still unsettled.

EXPERIMENTAL.

1 : 8-Naphthalyl chloride was prepared after the method of Mason (*loc. cit.*). It is advantageous to use glacial phosphoric acid as grease for the ground joint in the bromine flask in order to prevent seizing. In addition to the properties already described, naphthalyl chloride is very soluble in benzene, hot or cold. Attempts to distil it under moderately reduced pressure lead to complete decomposition

as mentioned by Mason, some carbonyl chloride being produced. The substance, however, distils unchanged at 195—200°/about 0·2 mm. when the operation is rapidly carried out on small quantities (about 10 g.).

Attempted Conversion into the Tautomeric Form.—When the acid chloride is heated for several hours with its own weight of powdered aluminium chloride in a sealed tube, no appreciable change occurs at about 86°, and complete decomposition takes place at about 115°. Since the substance can even be distilled without the other tautomeric form being produced, it is evident that the acid chloride has no great tendency to exhibit tautomerism.

1-*Cyano*-8-*naphthoic Acid.*—A solution of naphthalyl chloride (10 g.) in benzene (150 c.c.) is filtered from a trace of anhydride, and a stream of dry ammonia passed into it for 2 hours with shaking and occasional heating. Reaction readily occurs and a copious grey precipitate is formed. The benzene filtrate smells strongly of ammonia, but evolves a large quantity of hydrogen chloride after 12 hours. This phenomenon is also observed when the ammonia has been passed for a much longer period, and seems to indicate that the acid chloride is not very reactive towards dry ammonia. Concentrated aqueous ammonia and a benzene solution of the acid chloride rapidly interact, but the product is naphthalic anhydride. The above-mentioned grey precipitate is collected and shaken with hot aqueous sodium carbonate, the filtered red solution is quickly cooled and acidified with acetic acid, and the naphthalic acid produced is collected; the filtrate is then strongly acidified with hydrochloric acid, whereupon about 3 g. of the crude *cyanonaphthoic acid* separate. It crystallises from benzene–light petroleum, or from nitrobenzene, in clusters of colourless needles. It is sparingly soluble in water, moderately easily soluble in most of the usual organic solvents, and melts indefinitely with decomposition at 210—250°; the product contains naphthalimide, m. p. 300° (Found: equiv., 196·8; N, 7·1. $C_{12}H_7O_2N$ requires equiv., 197; N, 7·1%).

Cyanonaphthoic acid is very reactive. It dissolves in cold concentrated sulphuric acid with a purple fluorescence, and is gradually converted into naphthalic anhydride (m. p. 274°; mixed m. p. 274°). It dissolves readily in cold dilute sodium hydroxide solution and in warm ammonia and sodium carbonate solutions, from which it is only partly precipitated by excess of acetic acid, but completely by mineral acid. The solution in any of the alkaline reagents mentioned, when boiled for some time, deposits a large amount of crystalline matter in the heat, and the cyanonaphthoic acid is rapidly destroyed. Probably salts of naphthalic acid and of the acid amide of naphthalic acid are produced. Attempts to methylate the cyanonaphthoic

acid with silver oxide and methyl iodide gave methyl naphthalate, m. p. 102° (mixed m. p. 102°).

1 : 8-*Naphthaldianilide.*—A dilute benzene solution of naphthalyl chloride is mixed with excess of aniline in benzene and the solid which slowly settles is collected after 24 hours. This is well washed with benzene and repeatedly with boiling water, and the dried substance is crystallised from nitrobenzene, from which it separates in minute, colourless needles melting with decomposition at 250—282° according to the rate of heating (Found : N, 7·9. $C_{24}H_{18}O_2N_2$ requires N, 7·65%). The substance is only sparingly soluble in low-boiling organic solvents.

1 : 8-*Naphthalbisdimethylanilide* is formed similarly, but in this case a large quantity of naphthalic anhydride is formed, which is removed by repeated extraction with boiling potassium hydroxide solution. 1 : 8-*Naphthalbisdimethylanilide* separates from nitrobenzene in minute prisms, melting sharply at 245—246° without decomposition (Found : N, 7·4. $C_{26}H_{22}O_2N_2$ requires N, 7·2%).

The authors wish to record their indebtedness to Dr. F. A. Mason and Mr. L. Rubenstein for advice and assistance in the preparation of naphthalyl chloride. One of them (W. D.) also wishes gratefully to acknowledge grants from the Research Fund Committee of the Chemical Society and the Government Grant Committee of the Royal Society, and a Senior Studentship from the Commissioners of the 1851 Exhibition, which have all been partly applied to the prosecution of the above work.

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CLV.—*Investigations in the Diphenyl Series. Part V. Derivatives of* 4-*Amino- and* 4-*Hydroxy-diphenyl.*

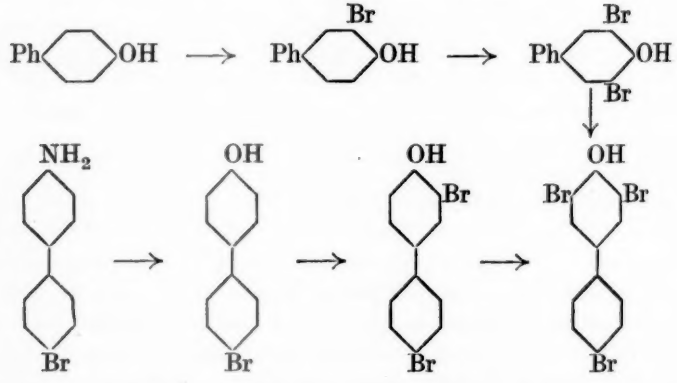
By FRANK BELL and PERCY HARRY ROBINSON.

SINCE dinitro-4-methylaminodiphenyl (Bell and Kenyon, J., 1926, 2711) is resistant to acetylating agents, it was inferred that the nitro-groups are in the 3 : 5-positions. This view is substantiated by the fact that 3-nitro-4-methylaminodiphenyl is readily acetylated. 3-Nitro-4-methylaminodiphenyl, which had previously been obtained by the oxidation of 3-nitro-4-dimethylaminodiphenyl (Garciá Banús and Ferrer Tomás, *Anal. Fís. Quím.*, 1921, **19**, 293), was advantageously prepared by the hydrolysis of 3-*nitro*-4-p-*toluenesulphonmethylamidodiphenyl*, obtained by nitration of the corre-

sponding amide. It appears that the orienting influence of the *p*-toluenesulphonmethylamido-group is very similar to that of the acetamido-group. This conclusion is supported by a comparison of the results of the nitration of *p*-toluenesulphonmethylanilide with that of acetanilide, since the ratio of *p* : *o* substitution is very approximately the same in both cases.

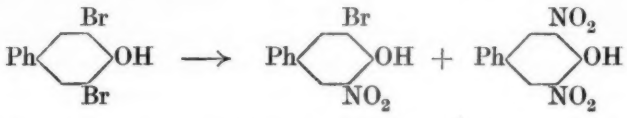
The further substitution of 3 : 4-derivatives of diphenyl is of considerable interest. On further nitration, 3-nitro-4-acetamido- (or dimethylamino-)diphenyl and 3-nitro-4-hydroxydiphenyl yield only 5-nitro-derivatives (Fichter and Sulzberger, *Ber.*, 1904, **37**, 878; Bell and Kenyon, *loc. cit.*; Garciá Banús and Guiteras, *Anal. Fís. Quím.*, 1923, **21**, 126), but 3-nitro-4-methoxydiphenyl, in addition, gives about 15% of the 4′-nitro-derivative (Bell and Kenyon, J., 1926, 3046). The somewhat surprising production of the 4′-bromo-derivative in the bromination of 4-acetamidodiphenyl (Scarborough and Waters, J., 1926, 558; Kenyon and Robinson, *ibid.*, p. 3050) suggested that the bromination of the above compounds might yield interesting results, and 3-nitro-4-acetamidodiphenyl has now been examined. The product consists mainly of the 5-bromo-derivative, together with some of the 5 : 4′-dibromo-derivative and small amounts of other products. No 4′-bromo-3-nitro-4-acetamidodiphenyl was isolated from the reaction mixture.

The bromination of 4-hydroxydiphenyl has now been shown to follow a normal course. Monobromination gives the 3-derivative, dibromination the 3 : 5-derivative, and tribromination the 3 : 5 : 4′-derivative. 4′-Bromo-4-hydroxydiphenyl was prepared from 4′-bromo-4-aminodiphenyl, and converted successively into 3 : 4′-dibromo- and 3 : 5 : 4′-tribromo-4-hydroxydiphenyl.



3 : 5-Dibromo-4-hydroxydiphenyl readily reacts with nitrous acid to give a complex mixture from which 5-bromo-3-nitro- and 3 : 5-

dinitro-4-hydroxydiphenyl have been isolated. This result is in marked contrast with that obtained by Raiford and Colbert (*J. Amer. Chem. Soc.*, 1925, **47**, 1456), who not only failed to isolate these products, but stated that the principal product is a nitrodibromophenol, m. p. 171°. Of this, we can discover no trace.



Experimental.

Nitration of p-*Toluenesulphonmethylanilide.*—10 G. were added to warm nitric acid (20 c.c.); vigorous reaction then occurred. The cooled mixture was filtered from an insoluble part (8·5 g.), and the filtrate poured into water. The precipitated gum (1·3 g.) crystallised from alcohol in prismatic needles, m. p. 126°, identical with *p*-toluenesulphonmethyl-2-nitroanilide (described below). The less soluble material was crystallised from alcohol, and separated into *p*-toluenesulphonmethyl-4-nitroanilide, m. p. 175—176° (identified by comparison with a specimen prepared from *p*-nitroaniline and by hydrolysis to 4-nitromonomethylaniline), and a further small crop of the 2-nitro-derivative.

p-*Toluenesulphon-2-nitroanilide*, prepared by the interaction of *o*-nitroaniline and *p*-toluenesulphonyl chloride in pyridine solution, crystallised from alcohol in prismatic needles, m. p. 110° (Found: C, 54·1; H, 4·2. $C_{13}H_{12}O_4N_2S$ requires C, 53·4; H, 4·1%). By methylation with methyl sulphate it gave p-*toluenesulphonmethyl-2-nitroanilide*, m. p. 126° (Found: C, 54·4; H, 4·5. $C_{14}H_{14}O_4N_2S$ requires C, 54·9; H, 4·6%).

Nitration of 4-p-*Toluenesulphonmethylamidodiphenyl.*—To 12·5 g., dissolved in acetic acid (125 c.c.) at 70°, was added nitric acid (*d* 1·5; 10 c.c.) in acetic acid (10 c.c.), and the whole was maintained at 70—75° for ¼ hour. On cooling, the liquid became filled with needles (11 g., m. p. 154—156°), which were filtered off and, after recrystallisation from acetic acid, had m. p. 157° (Found: C, 63·2; H, 4·9. $C_{20}H_{18}O_4N_2S$ requires C, 62·8; H, 4·7%). The filtrate, when poured into water, gave gummy material (4·5 g.). The main product of the reaction was identical with 3-*nitro*-4-p-*toluenesulphonmethylamidodiphenyl*, prepared by the methylation of 3-nitro-4-*p*-toluenesulphonamidodiphenyl.

3-*Nitro*-4-*methylaminodiphenyl.*—A solution of 3-nitro-4-*p*-toluenesulphonmethylamidodiphenyl (10 g.) in sulphuric acid (20 c.c.) was after ½ hour poured on ice and neutralised with ammonia, and

the resulting precipitate was filtered off and crystallised from alcohol. 3-Nitro-4-methylaminodiphenyl forms orange-red needles, m. p. 112°.

3-*Nitro*-4-*nitrosomethylaminodiphenyl*, prepared by the addition of a slight excess of sodium nitrite to a solution of 3-nitro-4-methylaminodiphenyl in acetic acid (10 parts), crystallised from alcohol in pale yellow needles, m. p. 87° (Found : C, 60·8; H, 4·4. $C_{13}H_{11}O_3N_3$ requires C, 60·7; H, 4·2%). Nitration converted it into 3 : 5-dinitro-4-nitrosomethylaminodiphenyl.

3-*Nitro*-4-*acetmethylamidodiphenyl*.—3-Nitro-4-methylaminodiphenyl was warmed on a water-bath with acetic anhydride, until the deep red colour of the solution faded to pale yellow. The solution was poured into water, and the gummy deposit dissolved in alcohol, from which it separated as a pale yellow, crystalline powder, m. p. 89° (Found : C, 66·8; H, 4·7. $C_{15}H_{14}O_3N_2$ requires C, 66·6; H, 5·2%).

Nitration of 4 : 4′-*Di*-p-*toluenesulphonamidodiphenyl*.—This compound (10 g.) was added slowly to nitric acid (*d* 1·4; 20 c.c.), and the mixture was diluted with acetic acid and filtered. 3 : 3′-*Dinitro*-4 : 4′-*di*-p-*toluenesulphonamidodiphenyl* crystallises from pyridine–ethyl alcohol in needles, m. p. 220° (Found : C, 53·8; H, 3·8. $C_{26}H_{22}O_8N_4S_2$ requires C, 53·6; H, 3·8%). It was hydrolysed by dissolving it in sulphuric acid (3 parts) and, after ½ hour, pouring the solution into water. Pure 3 : 3′-dinitrobenzidine, m. p. 275°, was obtained when the product was crystallised from pyridine–ethyl alcohol.

Bromination of 3-*Nitro*-4-*acetamidodiphenyl*.—To a solution of 3-nitro-4-acetamidodiphenyl (17 g.) in acetic acid (70 c.c.), bromine (11 g.) in acetic acid (5 c.c.), and ferric chloride (1 g.) were added. The mixture was heated on a water-bath for 10 hours, cooled, and filtered from a deposit (13 g.) which consisted mainly of the hydrobromides of bases produced by hydrolysis. The filtrate was poured into water; the gummy deposit (8 g.) thus obtained crystallised from alcohol in needles, m. p. 93—95° (Found : C, 50·4; H, 3·0. $C_{14}H_{11}O_3N_2Br$ requires C, 50·2; H, 3·3%). The hydrobromides were decomposed by boiling water and the mixture of amines obtained was acetylated. The acetyl derivatives were readily separated by crystallisation from alcohol into a less soluble portion, m. p. 140—150°, and a more soluble portion, m. p. 85—95°. The former, after crystallisation from carbon tetrachloride and then from alcohol, formed long, yellow needles, m. p. 153° (Found : C, 40·0; H, 2·4. $C_{14}H_{10}O_3N_2Br_2$ requires C, 40·5; H, 2·4%), whilst the latter, after repeated crystallisation, gave pure (5 ?)-*bromo*-3-*nitro*-4-*acetamidodiphenyl*, m. p. 94—95°. The compound, m. p.

153°, is probably 5 : 4′-*dibromo*-3-*nitro*-4-*acetamidodiphenyl*, since it was also obtained by the bromination of 4′-bromo-3-nitro-4-acetamidodiphenyl as follows. To a hot solution of 4′-bromo-4-acetamidodiphenyl (3 g.) in acetic acid (30 c.c.) was added nitric acid (*d* 1·5; 2 c.c.) in acetic acid (2 c.c.). After ½ hour, the mixture was allowed to cool; 4′-bromo-3-nitro-4-acetamidodiphenyl, m. p. 197—200°, then separated. This compound (2·4 g.), acetic acid (30 c.c.), bromine (1·6 g.), and ferric chloride were warmed together until hydrogen bromide ceased to be evolved. On cooling, the liquid filled with orange needles, m. p. 151—153°.

In addition to the 5- and 5 : 4′-bromo-derivatives, there was isolated a trace of a compound which crystallised from alcohol in colourless needles, m. p. 210—213° (Found : C, 45·6; H, 3·1; N, 3·8%).

4′-*Bromo*-4-*aminodiphenyl* was prepared by Le Fèvre and Turner's method (J., 1926, 2045) and characterised by means of its p-*toluenesulphonyl* derivative, which crystallised from alcohol in needles, m. p. 174° (Found : C, 57·2; H, 3·65. $C_{19}H_{16}O_2NBrS$ requires C, 56·7; H, 4·0%).

4′-*Bromo*-4-*hydroxydiphenyl*.—4′-Bromo-4-aminodiphenyl (10 g.) was dissolved in boiling dilute hydrochloric acid (700 c.c. of 1%), the solution rapidly cooled to 5—10°, and sodium nitrite (3 g.) added. After ½ hour, the solution was filtered, dilute sulphuric acid added, and steam passed in. The precipitate which formed was filtered off and extracted with boiling dilute aqueous sodium hydroxide. The extract was acidified with hydrochloric acid and the crude bromophenol precipitated was filtered off and crystallised from alcohol. 4′-*Bromo*-4-*hydroxydiphenyl* forms plates, m. p. 164—166° (Found : C, 57·6; H, 3·8. $C_{12}H_9OBr$ requires C, 57·8; H, 3·6%).

3 : 4′-*Dibromo*-4-*hydroxydiphenyl*.—To a warm solution of 4′-bromo-4-hydroxydiphenyl (10 g.) in chloroform (90 c.c.) was added bromine (6·5 g.) in chloroform (10 c.c.). The chloroform solution was evaporated to a small bulk and then diluted with light petroleum. On cooling, hard, stellate masses, m. p. 117°, were formed (Found : C, 44·2; H, 2·7. $C_{12}H_8OBr_2$ requires C, 43·9; H, 2·4%).

3 : 5 : 4′-*Tribromo*-4-*hydroxydiphenyl*, prepared as described above from 4′-bromo-4-hydroxydiphenyl (7·4 g.) and bromine (10·8 g.), crystallised from chloroform in stout needles, m. p. 159° (Found : C, 35·8; H, 1·9. $C_{12}H_7OBr_3$ requires C, 35·4; H, 1·7%).

3 : 4′-*Dibromo*-5-*nitro*-4-*hydroxydiphenyl*.—To a warm solution of 3 : 4′-dibromo-4-hydroxydiphenyl (3·2 g.) in acetic acid (20 c.c.) was added nitric acid (*d* 1·4; 0·8 c.c.) in acetic acid (10 c.c.). The

solution rapidly filled with small needles; these, after crystallisation from chloroform, had m. p. 189° (Found: C, 38·9; H, 2·0. $C_{12}H_7O_3NBr_2$ requires C, 38·6; H, 1·9%).

3-*Bromo*-4-*hydroxydiphenyl*.—To a warm solution of 4-hydroxydiphenyl (7·8 g.) in chloroform (70 c.c.) was added bromine (7·4 g.) in chloroform (10 c.c.). After partial evaporation of the chloroform, and dilution with light petroleum, the liquid filled with needles of 3-*bromo*-4-*hydroxydiphenyl*, m. p. 96° (Found: C, 57·8; H, 3·5. $C_{12}H_9OBr$ requires C, 57·8; H, 3·6%).

3 : 5-Dibromo-4-hydroxydiphenyl, obtained in quantitative yield by using 14·8 g. of bromine in the previous preparation, crystallised from chloroform–light petroleum in needles, m. p. 91—94° (Raiford gives m. p. 96°).

Oxidation of 4 g. with alkaline permanganate gave a trace of *p*-bromobenzoic acid, and we were unable to eliminate the small amount of impurity which gives rise to this acid. The dibromophenol is, however, readily characterised as its p-*toluenesulphonyl* derivative, which crystallises from acetic acid in needles, m. p. 132° (Found: C, 47·5; H, 2·6. $C_{19}H_{14}O_3Br_2S$ requires C, 47·3; H, 2·9%). Further bromination in chloroform slowly converted this dibromophenol into 3 : 5 : 4′-tribromo-4-hydroxydiphenyl (see above).

Action of Nitrous Acid on 3 : 5-*Dibromo*-4-*hydroxydiphenyl*.—Various amounts of sodium nitrite (1—2 mols.) and acetic acid were tried, and the following is a typical experiment. To a solution of the dibromophenol (10·9 g.) in acetic acid (100 c.c.), sodium nitrite (3·6 g.), dissolved in the minimum quantity of water, was added. After ¼ hour, the mixture was warmed on the steam-bath for a few minutes and then poured into water. The oily product obtained slowly solidified; after being dried, and fractionally crystallised from chloroform, it gave two pure products. The less soluble formed yellow, lustrous plates, m. p. 152° (Found: C, 55·7; H, 3·0%), identical with 3 : 5-dinitro-4-hydroxydiphenyl (Calc.: C, 55·4; H, 3·1%) prepared by the method of Garciá Banús and Guiteras (*loc. cit.*). The more soluble portion, which formed golden-yellow needles, m. p. 76°, was 5-*bromo*-3-*nitro*-4-*hydroxydiphenyl* (Found: C, 49·1; H, 3·1. $C_{12}H_8O_3NBr$ requires C, 49·0; H, 2·7%). Only gummy products were formed when 3 : 5-dibromo-4-hydroxydiphenyl was treated with nitric acid (1 mol.).

Action of Nitrous Acid on 3 : 5 : 4′-*Tribromo*-4-*hydroxydiphenyl*.—To this tribromophenol (2·2 g.) in hot acetic acid (33 c.c.) was added sodium nitrite (0·6 g.), and the solution was poured into water. The bulk of the product consisted of 5 : 4′-dibromo-3-nitro-4-hydroxydiphenyl (above).

Action of Nitric Acid on 3-*Bromo*-4-*hydroxydiphenyl*.—To this

bromophenol (5·2 g.) in acetic acid (25 c.c.) was added nitric acid (1·5 c.c.) in acetic acid (10 c.c.). The reaction was completed by warming, the mixture poured into water, and the precipitated mass filtered off and fractionally crystallised from chloroform–light petroleum. It was thus separated into 3 : 5-dinitro-4-hydroxydiphenyl, 5-bromo-3-nitro-4-hydroxydiphenyl, and a small amount of 5-bromo-3 : 4′-dinitro-4-hydroxydiphenyl (see below).

3-*Bromo*-4′-*nitro*-4-*hydroxydiphenyl*.—To a suspension of 4′-nitro-4-hydroxydiphenyl (4 g.) in boiling chloroform (70 c.c.) was added bromine (3 g.) in chloroform (10 c.c.), and the resultant solution was evaporated. The residue crystallised from aqueous acetic acid as a pale yellow powder, m. p. 132° (Found: C, 49·6; H, 3·0. $C_{12}H_8O_3NBr$ requires C, 49·0; H, 2·7%).

5-*Bromo*-3 : 4′-*dinitro*-4-*hydroxydiphenyl*.—To 3-bromo-4′-nitro-4-hydroxydiphenyl (3 g.) in warm acetic acid (20 c.c.) was added nitric acid (0·8 c.c.) in acetic acid (5 c.c.). The liquid immediately filled with golden-yellow needles, which, after crystallisation from acetic acid, melted at 218° (Found: C, 42·1; H, 2·4. $C_{12}H_7O_5N_2Br$ requires C, 42·5; H, 2·1%).

In conclusion, the authors wish to express their thanks to Dr. J. Kenyon for his interest in this work, and to the Advisory Council of the Department of Scientific and Industrial Research for a grant made to one of them.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, March 1st*, 1927.]

CLVI.—*Higher Substitution Products of 4-Aminodiphenyl.*

By HAROLD ARCHIBALD SCARBOROUGH and WILLIAM ALEXANDER WATERS.

THE study of the substitution reactions of the monoacid bases of the diphenyl series (J., 1926, 557; this vol., p. 89) has been extended to include an examination of the products obtained by the further substitution of 3-chloro-4-aminodiphenyl, 3-nitro-4-aminodiphenyl, and their acetyl derivatives.

In every case, the introduction of one more substituent group into the free base proceeds with great ease at room temperature, and leads invariably to a product substituted in the 5-position. Thus 3-chloro- and 3-nitro-4-aminodiphenyl, on treatment with bromine in dilute acetic acid solution, yield 3-chloro-5-bromo-4-aminodiphenyl and 5-bromo-3-nitro-4-aminodiphenyl respectively. The introduction of any further substituent requires more drastic

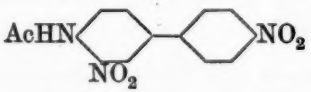
methods, particularly in the case of the 5-bromo-3-nitro-4-aminodiphenyl, and the substituent enters the 4′-position.

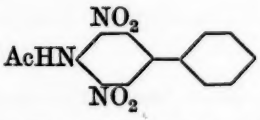
In contrast to the observed reactivity of the free bases, it is found that the further substitution of their acetyl derivatives proceeds only at high temperatures, in the presence of catalysts, or under other drastic conditions, and in every case the substituent enters the 4′-position. Thus 3-chloro-4-acetamidodiphenyl can be monobrominated by the use of pyridine as a catalyst, and mononitrated by dissolving it in nitric acid (*d* 1·4) at room temperature.

By still more drastic treatment, it has been found possible to obtain a dinitro-substitution product, which is probably 3-chloro-5 : 4′-dinitro-4-acetamidodiphenyl, but there is no evidence of the formation of a dibromo-derivative, although the free base, 3-chloro-4′-bromo-4-aminodiphenyl, can be brominated with great ease to yield 3-chloro-5 : 4′-dibromo-4-aminodiphenyl.

3-Nitro-4-acetamidodiphenyl is still less reactive, for it is only partly chlorinated by the prolonged action of dry chlorine in boiling glacial acetic acid solution, whilst bromination with the use of pyridine as a catalyst leads to only a 60% yield of 4′-bromo-3-nitro-4-aminodiphenyl, identical with the product obtained by Le Fèvre and Turner (J., 1926, 2045) by the nitration of 4′-bromo-4-acetamidodiphenyl.

The dinitration of 4-acetamidodiphenyl leads to a quantitative yield of 3 : 4′-dinitro-4-acetamidodiphenyl (I), for which the structure of 3 : 5-dinitro-4-acetamidodiphenyl (II) had previously been suggested by Fichter and Sulzberger (*Ber.*, 1904, **37**, 878) without any proof having been given.

(I.) 



(II.)

The corrected structure (I) follows from the fact that the substance can be oxidised to *p*-nitrobenzoic acid.

From an examination of all recorded disubstitution reactions of 4-aminodiphenyl and its derivatives it may be seen that, whereas the free base yields derivatives substituted in the 3- and 5-positions, the acetyl derivative yields derivatives substituted in the 3- and 4′-positions.

This difference in mode of reaction must probably be ascribed to the inhibiting effect of the acetyl group, which decreases the activating power of the amino-group on the adjacent 3- and 5-positions in the same ring to such an extent that the normal ortho-para directive influence of the phenyl group predominates and leads to substitution in the 4′-position.

Although a substituted amino-group normally leads to substitution in the same ring in the first instance, thus showing that the difference in the type of the reaction cannot be solely due to steric hindrance, yet there are recorded instances in which substitution takes place initially in the 4′-position in the opposite ring. Of these, the bromination of 4-acetamidodiphenyl and the nitration of 2-acetamidodiphenyl have already been noted by the authors, and it has been suggested (J., 1926, 557) that these differences may possibly arise in consequence of differences of mechanisms of the substitution reactions. In particular, it has been thought possible that the initial rapid substitution in the same ring as an acetamido-group may be brought about by a mechanism involving an initial attack on the " side chain " followed by a migration reaction (which has been proved to yield the same type of product), and that the far slower substitution in the opposite ring might be due to a direct attack of the substituting group on the aromatic nucleus.

In an attempt to test this hypothesis, an examination of the reactivity towards substitution reagents of diacetyl-4-aminodiphenyl and of 4-phthalimidodiphenyl, which do not contain any hydrogen atom available for indirect attack, has been carried out. In each case it has been found that the reactivity of the molecule was still further decreased by the complete substitution of the amino-group, but unfortunately it has not been possible to isolate any definite substitution products.

4-Diacetylaminodiphenyl could not be attacked under conditions which did not first bring about hydrolysis of at least one of the acetyl groups, whilst 4-phthalimidodiphenyl was found to be too insoluble in the common reagents to be attacked except under conditions which lead to complete decomposition.

It may be noted, however, that the nitration of 4-benzylideneaminodiphenyl (Bell and Kenyon, J., 1926, 2707) and of 4-diphenylyltrimethylammonium nitrate (Vorländer, *Ber.*, 1925, **58**, 1893) in the 4′-position affords direct support for the view that substitution in the 4′-position is a direct reaction which will occur preferentially when indirect substitution is precluded.

As the disubstitution of 4-acetamidodiphenyl would seem to lead generally to substitution in the opposite ring, it would appear that the presence of a substituent group in the adjacent 3-position must also inhibit further substitution in the same ring. In accordance with the statement of Chattaway and Dowden (J., 1924, **125**, 1195) that the migration of a *N*-halogeno-derivative of a substituted acetanilide proceeds less and less readily as the number of substituent groups, especially nitro-groups, is increased, it may be suggested that the observed effect is due to the inhibition of any indirect reactions.

The effect of the nitro-group in 3-nitro-4-acetamidodiphenyl is most marked, for it would seem that not only does it prevent further substitution from taking place in the same ring, but also that it decreases the velocity of substitution in the other ring. This effect is in agreement with the known general effect of the nitro-group in making substitution more difficult to carry out, and it may be used to provide an explanation of the cases of unsymmetrical substitution in the diphenyl series which have been investigated recently.

For example, in the substitution of 4 : 4′-dichlorodiphenyl (compare Le Fèvre and Turner, J., 1926, 476, 2041) the C_6H_4Cl-group in the first instance has a stronger directive influence than the chlorine atom, and thus substitution occurs in the 2-position, but in the resultant compound the nitro-group has so reduced the directive power of the substituted phenyl group $C_6H_3(NO_2)Cl$· that the chlorine atom has the predominating directive influence, and in consequence a 3′-substituted derivative is produced.

The unsymmetrical nitration of diphthalylbenzidine may be explained similarly, and it may be noted that here also the phthalyl group plays the part of an inhibitor, in enabling the substituted phenyl group (—C_6H_4·N:Phth) to have a more powerful directive influence than the substituted amino-group (— N:Phth) in the first instance (compare Brady, Quick, and Welling, J., 1925, **127**, 2265).

Experimental.

3-Chloro-5-bromo-4-aminodiphenyl.—3-Chloro-4-aminodiphenyl (J., 1926, 560), dissolved in cold glacial acetic acid, containing an excess of powdered anhydrous sodium acetate, was treated with bromine (1 mol.) as a 10% solution in the same solvent. The product was separated after 5 minutes by pouring the mixture into water; it crystallised from alcohol in colourless needles, m. p. 107° (Found : 0·1515 g. gave 0·1774 g. of silver halides. Calc. weight, 0·1776 g.). The *benzoyl* derivative crystallised from methyl alcohol in fine needles, m. p. 222° (Found : 0·1633 g. gave 0·1401 g. of silver halides. Calc. weight, 0·1400 g.).

3-Chloro-5-bromodiphenyl, obtained from the base by the elimination of the amino-group in the usual manner, formed pale yellow needles, m. p. 29°, b. p. 225°/30 mm. (Found : 0·2283 g. gave 0·2846 g. of silver halides. Calc. weight, 0·2827 g.). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded 3-chloro-5-bromobenzoic acid (m. p. 193°).

3-Chloro-5 : 4′-dibromo-4-aminodiphenyl.—3-Chloro-5-bromo-4-aminodiphenyl was boiled for 3 hours with an excess of bromine in glacial acetic acid solution. The solid which was separated by

pouring the mixture into water proved to be partly acetylated, and therefore was hydrolysed by boiling it for 6 hours with alcoholic hydrochloric acid. The pure base then separated, and crystallised from alcohol in long needles, m. p. 129° (Found : 0·2010 g. gave 0·2885 g. of silver halides. Calc. weight, 0·2888 g.). By boiling this base for 8 hours with acetic acid and acetic anhydride, the *diacetyl* derivative was obtained, crystallising from dilute acetic acid in white needles, m. p. 147° (Found : C, 42·9; H, 2·8. Calc. : C, 43·05; H, 2·7%. 0·1716 G. gave 0·2007 g. of silver halides. Calc. weight, 0·2013 g.).

3-*Chloro*-4′-*bromo*-4-*acetamidodiphenyl*.—5 G. of 3-chloro-4-acetamidodiphenyl (*loc. cit.*), 10 g. of anhydrous sodium acetate, and 1 c.c. of pyridine were intimately mixed together, 5 c.c. of bromine were added slowly, and the mixture was heated at 100° for 3 hours. The product was separated from the reaction mixture in 60% yield by repeated crystallisation from methyl alcohol and from dilute acetic acid, and formed white needles, m. p. 185° (Found : 0·1600 g. gave 0·1630 g. of silver halides. Calc. weight, 0·1633 g.). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded *p*-bromobenzoic acid (m. p. 252°). The corresponding *base*, obtained by boiling the acetyl derivative for 4 days with 20% alcoholic hydrochloric acid, crystallised from methyl alcohol in white needles, m. p. 108° (Found : 0·1208 g. gave 0·1421 g. of silver halides. Calc. weight, 0·1417 g.). The base on warming with bromine in acetic acid yielded 3-chloro-5 : 4′-dibromo-4-aminodiphenyl which, alone or mixed with the product obtained by the alternative method, melted at 129°.

3-*Chloro*-4′-*nitro*-4-*acetamidodiphenyl*.—3-Chloro-4-acetamidodiphenyl was gradually dissolved in nitric acid (*d* 1·4) at room temperature, and after ½ hour the solution was poured on ice. The solid produced was washed with dilute ammonia and dissolved in a large volume of alcohol, from which it was deposited, on cooling, in fine yellow needles, m. p. 220·5° (Found : N, 9·4; Cl, 12·1. $C_{14}H_{11}O_3N_2Cl$ requires N, 9·6; Cl, 12·2%). On oxidation with chromic anhydride in glacial acetic acid solution, *p*-nitrobenzoic acid (m. p. 240°) was produced.

3-*Chloro*-5 : 4′-*dinitro*-4-*acetamidodiphenyl*.—3-Chloro-4-acetamidodiphenyl was gradually dissolved in nitric acid (*d* 1·5) at room temperature, and after 3 hours the solution was poured on ice. The solid produced was washed with dilute ammonia and extracted with alcohol; the residue crystallised from a large volume of methyl alcohol in fine, pale yellow needles, m. p. 250° (Found : N, 12·7; Cl, 10·55. $C_{14}H_{10}O_5N_3Cl$ requires N, 12·5; Cl, 10·55%). The substance was not oxidised by boiling with chromic anhydride in

glacial acetic acid solution. Such stability is characteristic of diphenyl derivatives containing a nitro-group in each ring.

5-Bromo-3-nitro-4-aminodiphenyl.—3-Nitro-4-aminodiphenyl (Fichter and Sulzberger, *loc. cit.*), dissolved in glacial acetic acid at 30–40°, was treated gradually with bromine (1 mol.) as a 10% solution in the same solvent. The product was separated after ½ hour by pouring the mixture into water, and, on attempted crystallisation from any of the common solvents, formed a very flocculent, orange-yellow mass of m. p. 99—101° which could not be freed from traces of more highly brominated substances (Found: Br, 30·1, 29·95. $C_{12}H_9O_2N_2Br$ requires Br, 27·3%). A similar mixture was obtained by the bromination of 3-nitro-4-aminodiphenyl in chloroform solution. An attempt at separation of a pure product by acetylation of the mixture was not successful.

By eliminating the amino-group in the usual manner, *5-bromo-3-nitrodiphenyl* was obtained in a pure form in more than 60% yield. It crystallised from alcohol in pale yellow needles, m. p. 72°, b. p. 240—250°/30 mm. (Found: Br, 28·8. $C_{12}H_8O_2NBr$ requires Br, 28·8%). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded 5-bromo-3-nitrobenzoic acid (m. p. 159—160°).

5 : 4′-Dibromo-3-nitro-4-aminodiphenyl.—5-Bromo-3-nitro-4-aminodiphenyl was heated at 100° for 6 hours with excess of bromine in glacial acetic acid solution, and the product, which was separated by pouring the mixture into water, was recrystallised from dilute acetic acid, forming red needles, m. p. 158° (Found: Br, 42·9. $C_{12}H_8O_2N_2Br_2$ requires Br, 43·0%). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded *p*-bromobenzoic acid (m. p. 253°).

The same product was obtained in poor yield by boiling 3-nitro-4-acetamidodiphenyl for 4 days with a large excess of bromine in glacial acetic acid solution.

4′-Chloro-3-nitro-4-acetamidodiphenyl.—Chlorine was passed for 4 hours into a solution of 10 g. of 3-nitro-4-acetamidodiphenyl and 20 g. of anhydrous sodium acetate in 200 c.c. of boiling glacial acetic acid. After cooling, excess of chlorine was removed with a current of air and water was added; a red gum was then deposited. This was extracted with hot alcohol and yielded 3 g. of bright yellow needles, m. p. 199° (Found: Cl, 12·15. $C_{14}H_{11}O_3N_2Cl$ requires Cl, 12·2%). On oxidation with chromic anhydride in glacial acetic acid solution, it yielded *p*-chlorobenzoic acid (m. p. 240°).

The corresponding *base* was obtained by boiling the acetyl derivative for 4 hours with 20% alcoholic hydrochloric acid, and crystallised from dilute acetone in scarlet needles, m. p. 174° (Found: Cl, 14·4. $C_{12}H_9O_2N_2Cl$ requires Cl, 14·3%).

4'-Bromo-3-nitro-4-acetamidodiphenyl.—5 G. of 3-nitro-4-acetamidodiphenyl, 10 g. of powdered anhydrous sodium acetate, and 1 c.c. of pyridine were intimately mixed together, 5 c.c. of bromine were gradually added, and the mixture was heated at 100° for 8 hours. The brominated product was isolated from the reaction mixture in 60% yield by extraction with acetone, and crystallised from that solvent in fine yellow plates, m. p. 207—208° (Found: Br, 24·0. Calc. for $C_{14}H_{11}O_3N_2Br$: Br, 23·9%). On oxidation with chromic anhydride in glacial acetic acid solution it yielded *p*-bromobenzoic acid (m. p. 253°). On hydrolysis with 20% alcoholic hydrobromic acid, the corresponding base was obtained, crystallising readily from dilute acetone in scarlet needles, m. p. 175° (Found: Br, 27·3. Calc. for $C_{12}H_9O_2N_2Br$: Br, 27·3%). Both the acetyl derivative and the base are obviously identical with the products obtained by Le Fèvre and Turner (J., 1926, 2045) by the nitration of 4'-bromo-4-acetamidodiphenyl.

3:4'-Dinitro-4-acetamidodiphenyl.—10 G. of 3-nitro-4-acetamidodiphenyl, dissolved in a mixture of 20 c.c. of concentrated sulphuric acid and 10 c.c. of glacial acetic acid at 0°, were treated during 2 hours with a mixture of 6 c.c. of fuming nitric acid and 14 c.c. of glacial acetic acid. After 24 hours, the product was poured on ice, and the yellow solid produced crystallised from glacial acetic acid and then from a large volume of acetone. From the latter solvent it formed long, pale yellow needles, m. p. 243—244° (corr.), obviously identical with the dinitro-4-acetamidodiphenyl, m. p. 240—241° (uncorr.), of Fichter and Sulzberger (*loc. cit.*). The same substance could be obtained more easily by dissolving 4-acetamidodiphenyl in cold fuming nitric acid and pouring the solution on ice after 30 minutes.

On prolonged oxidation with chromic anhydride in glacial acetic acid solution, *p*-nitrobenzoic acid (m. p. 240—241°) was produced, showing conclusively that the second nitro-group had entered the 4'- and not the 5-position.

The corresponding *base* was obtained by boiling 5 g. of the acetyl derivative with a mixture of 10 c.c. of concentrated sulphuric acid and 200 c.c. of alcohol for 2 days. It crystallised from a large bulk of alcohol in orange plates, m. p. 233—234°, corresponding exactly in properties with the base of Fichter and Sulzberger.

3:4'-Dinitrodiphenyl, obtained from the base by the elimination of the amino-group in the usual manner, crystallised from acetone in pale yellow needles, m. p. 189° (Found: N, 11·5. Calc.: N, 11·5%). Mention has already been made of the use of this compound for structure determination (this vol., p. 96).

Diacetyl-4-aminodiphenyl was obtained by boiling 4-acetamido-

diphenyl (10 g.) with acetic anhydride (50 c.c.) and anhydrous sodium acetate (5 g.) for 6 hours. It crystallised from light petroleum (b. p. 60—80°) in fine, white needles, m. p. 121° (Found: C, 75·55; H, 6·0. $C_{16}H_{15}O_2N$ requires C, 75·85; H, 5·9%).

It was not attacked by chlorine in cold 5% solution, but was hydrolysed on warming in presence of chlorine. There was no action on warming with 1 mol. of bromine in presence of anhydrous sodium acetate and a drop of pyridine, but complete decomposition occurred when a large excess of bromine was used.

On dissolving the diacetyl compound in nitric acid (*d* 1·4) at 0° and pouring the solution into ice and water after 10 minutes, a nitrated mixture was formed from which were separated pure specimens of 3-nitro-4-(mono)acetamidodiphenyl, m. p. 132°, and 3 : 4′-dinitro-4-(mono)acetamidodiphenyl, m. p. 244°; both were identified by mixed melting-point determinations with specimens obtained by the normal methods, and occurred in such quantities as to correspond to more than 70% of the theoretical yield of nitrated products.

4-*Phthalimidodiphenyl* was prepared by heating equivalent quantities of phthalic anhydride and 4-aminodiphenyl at 160° for 6 hours. It was a white powder, m. p. 288°, almost insoluble in all low-boiling solvents, but could be purified by long-continued extraction, in a Soxhlet apparatus, with boiling benzene. For analysis, it was separated twice from a large bulk of toluene and finally from xylene (Found: C, 80·3; H, 4·3. $C_{20}H_{13}O_2N$ requires C, 80·25; H, 4·4%).

The substance was insoluble in fuming nitric acid at room temperature, and was not attacked by bromine in presence of pyridine at 100°. It was decomposed completely by nitration in a large volume of concentrated sulphuric acid.

All the m. p.'s recorded in this paper have been corrected, and where necessary the identity of a substituted benzoic acid has been established by the "mixed m. p." method.

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THE UNIVERSITY CHEMICAL LABORATORIES,
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CLVII.—*The Iodination of* o-*Nitrophenol.*

By HERBERT HENRY HODGSON.

HÜBNER (*Ber.*, 1874, **7**, 461) described, but did not analyse, two iodonitrophenols, termed by him α and β, m. p. 90—91° and 66—67°, respectively, which he obtained by iodinating *o*-nitrophenol in glacial acetic acid in presence of mercuric oxide, and separated by fractionally crystallising their potassium salts from alcohol. The α-compound is stated to be only slowly volatile in steam, the β much more readily, and both were assumed to be monoiodonitrophenols.

In Beilstein's "Organische Chemie" (II, p. 700), the α- and the β-compound are recorded as 5(?)-iodo-2-nitrophenol and 6(?)-iodo-2-nitrophenol, respectively. Roberts (J., 1923, **123**, 2708) doubts whether they are pure substances, since neither is identical with his 4-iodo-2-nitrophenol (m. p. 80—81°) or with Brenans's 2-iodo-6-nitrophenol (m. p. 110°) or2-iodo-4-nitro phenol (m. p. 86—87°) (*Compt. rend.*, 1902, **134**, 357). Keimatsu (*J. Pharm. Soc. Japan*, 1924, No. 507, 319) regards the Hübner compounds as 3- and 4-iodo-2-nitrophenols. If this is so, the former would be an example of an unexpected type of iodination.

The present author, having already prepared 5-iodo-2-nitrophenol (m. p. 96°) and 3-iodo-2-nitrophenol (m. p. 73·5°) (this vol., p. 630) is in possession of the necessary standards for the solution of this problem. He has found that in all cases of direct iodination of *o*-nitrophenol with the aid of mercuric oxide, whether the quantity of iodine taken is less than, equal to, or greater than that required for mono-iodination according to the equation $2NO_2{\cdot}C_6H_4{\cdot}OH + 2I_2 + HgO = 2NO_2{\cdot}C_6H_3I{\cdot}OH + HgI_2 + H_2O$, di-iodination occurs to a considerable extent and various quantities of mercurous salts are also produced. Hübner's α- and β-compounds have proved to be 4 : 6-di-iodo-2-nitrophenol and 4-iodo-2-nitrophenol, respectively, mixed with small quantities of 6-iodo-2-nitrophenol. The mono-iodo-2-nitrophenols are all readily volatile in steam.

The considerable tendency toward di-iodination, and the formation of 4-iodo-2-nitrophenol in excess of that of the 6-iodo-isomeride, indicate that the initial mono-iodination of *o*-nitrophenol occurs preferentially in position 4. No indication of the presence of 3-iodo-2-nitrophenol has been detected.

EXPERIMENTAL.

For purposes of comparison, 6-iodo-2-nitrophenol (m. p. 110°) and 4-iodo-2-nitrophenol (m. p. 80—81°) were prepared by direct

nitration of 2- and 4-iodophenols, respectively; 4 : 6-di-iodo-2-nitrophenol (m. p. 98°) by direct iodination of *o*-nitrophenol in glacial acetic acid in presence of yellow mercuric oxide, by iodination of 4-iodo- and 6-iodo-2-nitrophenols, and by Roberts's method (*loc. cit.*); 6-iodo-2 : 4-dinitrophenol (m. p. 106°) and 4-iodo-2 : 6-dinitrophenol (m. p. 113°) by direct iodination of 2 : 4- and 2 : 6-dinitrophenols, respectively, and also by the dinitration of 2- and 4-iodophenols by Hodgson and Moore's method for the dinitration of *m*-chlorophenol (J., 1925, **127**, 1601).

Iodination by Hübner's Method.—A solution of *o*-nitrophenol (2 mols.) and iodine (2 mols.) in glacial acetic acid, while being vigorously shaken, was treated gradually with yellow mercuric oxide until the iodine had disappeared. The mixture was then filtered, and the filtrate diluted with water to precipitate the iodonitrophenols. These were washed by decantation, and treated with warm aqueous potassium hydroxide, and the filtered solution was evaporated to dryness. The solid residue was boiled with alcohol several times, and the combined extracts were allowed to cool; long, red needles were deposited, which were continually removed (α) until more tabular and yellower crystals began to appear (β). The two batches, α and β, were each treated with sulphuric acid, and then steam-distilled until the more volatile products had passed over. In each case, the slowly volatile material was crystallised several times from dilute alcohol, the melting point being thus raised from 94° to 98° (Found: I, 65·1. Calc. for $C_6H_3O_3NI_2$: I, 64·9%). Mixed with authentic 4 : 6-di-iodo-2-nitrophenol, the substances again melted at 98°. The potassium salts of these two compounds were alike in every way and different from the potassium salt of any of the monoiodo-2-nitrophenols.

The steam-volatile product in each case was recrystallised from alcohol until the m. p. had been raised from about 63° to 78° (Found for the compounds from the α- and the β-batch, respectively: I, 48·2, 48·1. Calc. for $C_6H_4O_3NI$: I, 47·9%). Mixed with authentic 4-iodo-2-nitrophenol, each compound melted at 79—80°, and the identity was further established (*a*) by iodination to 4 : 6-di-iodo-2-nitrophenol, (*b*) by nitration to 4-iodo-2 : 6-dinitrophenol, and (*c*) by nitration to picric acid without 3-iodo-2 : 4 : 6-trinitrophenol being detected.

The residual potassium salt from the original alcoholic extract (above) was suspended in dilute sulphuric acid and submitted to steam-distillation. The volatile product, after several crystallisations from alcohol, melted at 102° (Found: I, 48·0. Calc. for $C_6H_4O_3NI$: I, 47·9%). Its identity with 6-iodo-2-nitrophenol was indicated by the like crystalline forms, and by the melting point

of a mixture of the two substances, and was confirmed (*a*) by iodination to 4 : 6-di-iodo-2-nitrophenol, (*b*) by nitration to 6-iodo-2 : 4-dinitrophenol, and (*c*) by trinitration to picric acid without 3-iodo-2 : 4 : 6-trinitrophenol being detected.

A slightly volatile product obtained in the above steam-distillation was 4 : 6-di-iodo-2-nitrophenol.

The same results were obtained when the iodination of *o*-nitrophenol was carried out at 40—50°; when iodine, dissolved in ether, was added in small portions at a time, and the mixture was shaken during the gradual addition of mercuric oxide until the iodine had disappeared; and when alcohol was employed instead of glacial acetic acid as solvent.

Modifications of Hübner's Method.—(*a*) Instead of the potassium salts being prepared, the water-precipitated iodonitrophenols were steam-distilled, and several fractions collected. The earlier ones contained a little 6-iodo-2-nitrophenol, but consisted mainly of 4-iodo-2-nitrophenol. The later fractions contained a little 4 : 6-di-iodo-2-nitrophenol, and the residue was a mixture of this compound with mercurous and mercuric salts.

(*b*) The iodination was carried out as described above (*a*), but half the quantity of iodine was used. The steam-distillate was collected in three fractions, which were filtered off and extracted with boiling alcohol. The extract of the first fraction left a residue containing mercurous iodide, and deposited, on cautious dilution, crystals of 6-iodo-2-nitrophenol followed by an oil. The latter was dissolved in aqueous sodium hydroxide, the alcohol removed, and the solution was acidified and very slowly steam-distilled. The first-runnings deposited *o*-nitrophenol on cooling. The second fraction was treated similarly and found to contain mercurous iodide and 4- and 6-iodo-2-nitrophenols. The third fraction contained these substances and also 4 : 6-di-iodo-2-nitrophenol.

The original residue consisted mainly of 4 : 6-di-iodo-2-nitrophenol mixed with mercuric iodide.

(*c*) In this experiment, twice the quantity of iodine was used. The steam-volatile product was only small in amount, had a high m. p., and contained mercury. The bulk of the reaction product was the very slightly volatile 4 : 6-di-iodo-2-nitrophenol.

Evidence of the Absence of 3-Iodo-2-nitrophenol.—The entire water-precipitated mixture of iodonitrophenols obtained in an experiment according to Hübner was washed, dried, and divided into three equal portions. One of these was mixed with *m*-iodophenol, another with 3-iodo-2-nitrophenol, and the two mixtures and the third portion were separately trinitrated, and the products were worked up, by the methods used in the trinitration of *m*-iodophenol

(*loc. cit.*, p. 634). The mixture containing *m*-iodophenol and that containing 3-iodo-2-nitrophenol each gave a sublimate of 3-iodo-2 : 4 : 6-trinitrophenol, but the third portion of the Hübner product gave only picric acid. This result indicates the absence of 3-iodo-2-nitrophenol from this product.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 7th*, 1927.]

CLVIII.—*The Action of Caustic Alkalis on the 3-Halogeno-4-nitrosodimethylanilines.*

By HERBERT HENRY HODGSON and JOHN SAMUEL WIGNALL.

IN view of the conversion of 4-nitroso-3-chloro- and -3-bromo-phenols into their tautomerides, the 3-chloro- and 3-bromo-benzoquinone-4-oximes (Hodgson and Moore, J., 1923, **123**, 2499; 1925, **127**, 2260), it appeared desirable to ascertain whether the latter substances could be produced directly by the action of alkali hydroxide on the 3-halogeno-4-nitrosodimethylanilines. This result was obtained with the 3-chloro- and the 3-bromo-compound, but 3-iodo-4-nitrosodimethylaniline lost iodine when boiled with aqueous alkali hydroxide.

3-*Iododimethylaniline* and its 4-*nitroso*-derivative do not appear to have been prepared before. An improved method is described for making the 3-halogenodimethylanilines. The purity of preparations of 3-bromo-4-nitrosodimethylaniline described in the literature has hitherto been in doubt.

EXPERIMENTAL.

Preparation of the 3-Halogenodimethylanilines.—The 3-halogenoaniline (1/20 g.-mol.), methyl alcohol (12 c.c.), and methyl sulphate (15 c.c.) are mixed together, heat being evolved. When this has abated, the mixture is heated for 6 hours in a sealed tube. Dimethylation of 3-chloro- and of 3-bromo-aniline occurs at 165°, but 3-iodoaniline requires a temperature of 175° (it chars at 185°). The product is poured into water and made faintly alkaline, and the oil thus liberated is quickly separated, since otherwise emulsification readily takes place. The oil is washed, dried with calcium chloride, and distilled.

The bulk of the 3-chlorodimethylaniline distils between 230° and 233° and has b. p. 231° (Stadel, *Ber.*, 1883, **16**, 32, and Joubert, *Bull. Soc. chim.*, 1874, **21**, 24, give b. p. 231°) (Found: Cl, 22·7. Calc.: Cl, 22·8%).

3-Bromodimethylaniline distils between 244—245° and at 175°/

120 mm., and has b. p. 245° (Wurster, *Ber.*, 1879, **12**, 1818, gives b. p. 259°) (Found: Br, 40·1. Calc.: Br, 40%).

3-*Iododimethylaniline* has b. p. 215—216°/190 mm., but decomposes when distilled under atmospheric pressure (Found: I, 51·6. $C_8H_{10}NI$ requires I, 51·4%).

The 3-halogenodimethylanilines are viscous liquids which dissolve slowly in dilute mineral acids, but readily in the concentrated acids and then remain in solution on dilution.

Preparation of the 3-*Halogeno*-4-*nitrosodimethylanilines.*—A solution of the 3-halogenodimethylaniline (1/20 g.-mol.) in concentrated hydrochloric acid (16 c.c.) is diluted with water (60 c.c.), cooled to 0°, and treated slowly with sodium nitrite (7 g. in 35 c.c. of water). After an hour's stirring the yellow hydrochloride of the 3-halogeno-4-nitrosodimethylaniline is collected, and the green base is liberated from it and crystallised from methyl alcohol. The three compounds all crystallise in dark green needles.

3-Chloro-4-nitrosodimethylaniline has m. p. 130° (decomp.) (Stadel and Joubert, *locc. cit.*, do not record the m. p.) (Found: Cl, 19·1. Calc.: Cl, 19·2%).

3-Bromo-4-nitrosodimethylaniline has m. p. 129° (decomp.). Wurster (*loc. cit.*) gives m. p. 145°, Vorländer and Siebert (*Ber.*, 1919, **52**, 283) give m. p. 116°, and Kharasch and Piccard (*J. Amer. Chem. Soc.*, 1920, **42**, 1855) give m. p. 148°. The purifying process employed by Kharasch and Piccard is unnecessary when the 3-bromodimethylaniline used has been prepared by the method described above, nitrosation then proceeding smoothly. The above product, m. p. 129°, after treatment according to Kharasch and Piccard, remained unchanged; it still melted at 129°, and did not give the Liebermann nitroso-reaction—the test of purity employed by those authors (Found: Br, 34·7. Calc.: Br, 34·9%). The presence of under-methylated or of unchanged amine appreciably interferes with the nitrosation, and the product then obtained resinifies when kept.

3-*Iodo*-4-*nitrosodimethylaniline* has m. p. 128° (decomp.) (Found: I, 46·1. $C_8H_9ON_2I$ requires I, 46·0%). Like the corresponding chloro- and bromo-analogues, it is soluble with difficulty in methyl or ethyl alcohol, benzene, toluene, or ether, and insoluble in light petroleum or carbon tetrachloride.

Action of Aqueous Alkalis on the 3-*Halogeno*-4-*nitrosodimethylanilines.*—3-Chloro- or 3-bromo-4-nitrosodimethylaniline is boiled with a large excess of 10% halogen-free aqueous sodium or potassium hydroxide until almost complete solution is attained, dimethylamine being expelled. The filtered solution, when rendered just acid in the cold, gives a precipitate of the almost colourless form of 3-chloro-

or 3-bromo-benzoquinone-4-oxime, m. p. 175° and 190°, respectively (Found: Cl, 22·4. Calc.: Cl, 22·5%. Found: Br, 39·6. Calc.: Br, 39·6%). Comparison of the products, recrystallised from benzene (m. p. 178° and 190°, respectively), with Hodgson and Moore's (*loc. cit.*) preparations made by direct nitrosation of 3-chloro- and 3-bromo-phenol, and subsequent conversion by means of alkalis, established identity.

3-Iodo-4-nitrosodimethylaniline is decomposed by the above treatment into compounds of indefinite character with elimination of iodine. No similar removal of halogen occurs with the 3-chloro- and the 3-bromo-compound.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 19th*, 1927.]

CLIX.—*Acid and Salt Effects in Catalysed Reactions. Part VIII. The Determination of Hydrolytic Velocity Coefficients from Isocatalytic Data. Reaction Velocities in Buffer Solutions and Compound Catalytic Catenaries.*

By HARRY MEDFORTH DAWSON.

IN accordance with the theory outlined in previous papers (see, *e.g.*, this vol., p. 461), the velocity of hydrolytic reactions * has a minimum value when the hydrogen-ion concentration is that given by the equation

$$[H^+]_i = \sqrt{k_{OH}K_w/k_h} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At this point the partial velocities due respectively to the hydrogen ion and the hydroxyl ion are equal, and the total ionic reaction velocity is given by

$$u_i = 2\sqrt{k_h k_{OH} K_w} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From these equations, the isocatalytic data $[H^+]_i$ and u_i can be calculated if the coefficients k_h and k_{OH} are known; or, alternatively, the derived equations

$$2k_h = u_i/[H^+]_i \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$2k_{OH} = u_i[H^+]_i/K_w \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$k_{OH}/k_h = [H^+]_i^2/K_w \quad . \quad . \quad . \quad . \quad . \quad (5)$$

enable the converse calculations to be made. It is apparent that the derivation of k_{OH} or k_{OH}/k_h involves a knowledge of the ionisation product of the solvent, but that this is not required for the determination of k_h.

* The term hydrolytic reaction is used in this paper for any reaction which is catalysed by both the hydrogen and the hydroxyl ion.

The consideration of hydrolytic reactions from the point of view of the experimental measurement of the four quantities k_h, k_{OH}, $[H^+]_i$ and u_i is a matter of some interest. For those reactions in which undissociated water molecules take no measurable part, the ionic reaction velocity u may be identified with the actually measured velocity (v) and it is with reactions of this type that the present paper is primarily concerned. The procedure followed in the determination of k_h and k_{OH} is well known, and it need only be mentioned that attempts to measure v_i and $[H^+]_i$ have been made for the most part by the use of buffer solutions of varying p_H value.

In general, it is not possible to determine each of the four quantities k_h, k_{OH}, v_i, and $[H^+]_i$ by direct measurement, but the hydrolysis of aliphatic esters affords instances in which this may be readily accomplished, so far as the time factor is concerned. When the velocities of reaction, as measured by k_h and k_{OH}, are very much smaller, the direct measurement of v_i and $[H^+]_i$ may be attended with difficulties, as, for instance, in the case of the hydrolysis of aromatic amides at the ordinary temperature.

For some reactions, the relations may be such that only one of the velocity coefficients can be measured in the ordinary way. If, for instance, the ratio k_{OH}/k_h is of the order of 10^5, it is obvious that only one of the coefficients can be obtained directly from experiment. Quite apart from the difference in the order of magnitude of the coefficients, the transition from acid to alkaline solution may be complicated by the incidence of other reactions, concurrent or consecutive, which interfere with the measurement of the reaction velocity in question. Such complications occur in the acetone–iodine reaction, for which the value of k_h can be determined quite conveniently, but since the ratio k_{OH}/k_h is about 40,000, it is apparent that the direct measurement of k_{OH} would not be a simple matter even under the most favourable conditions. In actual fact, the measurement is precluded by the circumstance that subsequent reactions, leading to the production of iodoform, effectively mask the relations which characterise the primary stage of the acetone–iodine reaction in solutions of $p_H > 6$. In this particular instance, however, it has been found possible to determine the value of $[H^+]_i$ from observations on the velocity of the autocatalysed reaction (Dawson and Powis, J., 1912, **101**, 1503; Dawson, this vol., p. 458), and by combining this with k_h, the values of v_i and k_{OH} may be derived from equations (3) and (4).

Other hydrolytic reactions are distinguished by the circumstance that the values of k_h and k_{OH} are both so large that neither can be determined directly. It is not improbable that many of the reactions associated with the phenomena of tautomerism, pseudo-acidity, etc.,

afford examples which belong to this group. In such cases, it may sometimes be possible to obtain the velocity coefficients from the measurements of v_i and $[H^+]_i$.

Reactions in Buffer Solutions.

Since the use of buffer solutions serves to provide the stabilised p_H conditions which are necessary for the determination of v_i and $[H^+]_i$ in the case of hydrolytic reactions, it is necessary to examine critically the factors which are involved in the employment of such solutions for this purpose. In the light of the results which have been described previously (Dawson and Carter, J., 1926, 2282), it cannot be assumed that the catalytic effect of the acid and salt in the buffer solution is negligible. If, for instance, the solution used is an acetate buffer of p_H 5, in which the total acetate concentration is $0{\cdot}02M$, the concentrations of the constituents for which catalytic activity has been demonstrated are $[H^+] = 10^{-5}$, $[OH^-] = 10^{-9}$, $[HA] = 6 \times 10^{-3}$, and $[A^-] = 14 \times 10^{-3}$. In other words, the concentrations of the acetic acid and of the acetate ion are, respectively, 6×10^6 and 14×10^6 times that of the hydroxyl ion. In such circumstances, the possible catalytic action of buffer constituents, other than the hydrogen and hydroxyl ions, cannot be ignored. It may, in fact, be shown that the use of buffer mixtures does not in general yield the isocatalytic data which are characteristic of the H^+–OH^- catenary.

For the sake of simplicity it will be assumed that the buffer mixture consists of a weak acid HA and its corresponding salt, and that the variation of p_H is brought about by altering the concentration of the salt whilst the concentration of the acid (c) is kept constant. If the acid is not too weak, and its concentration not too small, the use of such a series of buffer solutions would give a point of minimum velocity characterised by values of $[H^+]_i$ and v_i given by the equations

$$[H^+]_i = \sqrt{k_a K c}/(k_h - k_m) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$v_i = 2\sqrt{(k_h - k_m)k_a K c} + k_m c \quad . \quad . \quad (7)$$

On the other hand, the isocatalytic data corresponding with the joint action of the hydrogen and hydroxyl ions are given by equations (1) and (2). In general, there will be a considerable difference between the two pairs of isocatalytic data. For the weaker acids which are commonly used in the preparation of buffer mixtures, k_m can be neglected in comparison with k_h and the difference between the two hydrogen-ion concentrations is essentially determined by the value of the ratio $k_a K c/k_{OH} K_w$. The difference would seem to disappear when $c = k_{OH} K_w/k_a K$. If the concentration of the acid

has this value, the *M.V.* point actually realised does not correspond, however, with equations (1) and (2), *i.e.*, with the H^+–OH^- catenary, but minimum velocity is attained at a greater hydrogen-ion concentration, which indeed is characteristic of a catenary curve for which the anionic catalytic effect is shared by the acid ions A^- and OH^-. This catenary may conveniently be described as a compound catenary.

The Compound Catenary.—Under conditions in which the total catalytic effect of the negative ions is shared by A^- and OH^-, the equation for the velocity of reaction may be written

$$v = k_h[H^+] + k_a[A^-] + k_{OH}[OH^-] + k_m[HA] + k_w[H_2O] \quad . \quad (8)$$

Since $[A^-] = K(c-[H^+])/[H^+]$ and $[OH^-] = K_w/[H^+]$, equation (8) may be put in the form

$$v = (k_h - k_m)[H^+] + (k_aKc + k_{OH}K_w)/[H^+] + k_mc + k_wc_w - k_aK \quad (9)$$

and if the concentration (c) of the acid HA is constant, it is evident that the reaction velocity passes through a minimum when

$$[H^+] = [H^+]_i = \sqrt{(k_aKc + k_{OH}K_w)/(k_h - k_m)} \quad . \quad (10)$$

and by substitution in (9) the minimum velocity is given by

$$v_i = 2\sqrt{(k_h - k_m)(k_aKc + k_{OH}K_w)} + k_mc + k_wc_w \quad (11)$$

if the negligibly small term k_aK be left out of account. The relations involved are of exactly the same kind as those which have been already described in connexion with the catalytic activity of acid–salt mixtures of the type cHA + xMA, and it is obvious that the total catalytic effects are such that the reaction velocity, in its dependence on p_H, can be represented by a catenary curve symmetrical with reference to the point defined by equations (10) and (11).

These compound catenaries form a continuous series limited on the one side by the H^+–OH^- catenary, and on the other by the simple catenaries which correspond with the acid–salt mixtures of the type cHA + xMA, for which the effect of the hydroxyl ion can be ignored. The relation between the hydrogen-ion concentrations $[H^+]_i'$ characteristic of the *M.V.* points on the compound catenaries and the hydrogen-ion concentration $[H^+]_i$ of the *M.V.* point on the H^+–OH^- catenary is given by

$$[H^+]_i'/[H^+]_i = \sqrt{(k_aKc + k_{OH}K_w)/k_{OH}K_w}$$

or

$$(p_H)_i - (p_H)_i' = \tfrac{1}{2}\log m \quad . \quad . \quad . \quad . \quad (12)$$

where $m = (k_aKc + k_{OH}K_w)/k_{OH}K_w$.

The numerical relations involved may be illustrated by reference to the acetone–iodine reaction for which the requisite data are

available. At 25° and an acetone concentration of 20 c.c. per litre, $k_{OH}K_w = 2{\cdot}0 \times 10^{-13}$, and for acetic acid $k_aKc = 832 \times 10^{-13}c$. In Table I are shown the values of c, $k_aKc \times 10^{13}$, $\sqrt{m}$, and $(p_H)_i - (p_H)_i'$.

TABLE I.

c	0	0·0001	0·0002	0·0005	0·001
$k_aKc \times 10^{13}$	0	0·08	0·16	0·42	0·83
$\sqrt{m}$	1·0	1·02	1·04	1·10	1·19
$(p_H)_i - (p_H)_i'$	0	0·01	0·02	0·04	0·08
c	0·002	0·005	0·01	0·02	0·05
$k_aKc \times 10^{13}$	1·66	4·15	8·3	16·1	41·6
$\sqrt{m}$	1·35	1·75	2·27	3·05	4·67
$(p_H)_i - (p_H)_i'$	0·13	0·24	0·36	0·48	0·67

When the concentration of the acetic acid reaches $0{\cdot}05N$, the catalytic effect of the hydroxyl ion can be almost neglected and the end of the series of compound catenaries may be said to have been reached. The non-interference of the H^+–A^- and H^+–OH^- catenaries may therefore be said to require that the difference in the p_H values of the *M.V.* points should not be less than about 0·7 p_H unit.

The gradual displacement of the *M.V.* point in passing from the H^+–OH^- catenary to the simple H^+–A^- catenaries is possibly best illustrated by reference to the exponential curves which represent the catalytic effect of the hydrogen ion on the one hand and the combined catalytic effect of the anions on the other. In adopting this method of comparing the relations, it is assumed that the acid HA is weak and that the coefficient k_m can be neglected in comparison with k_h. In these circumstances, the partial ionic reaction velocities are given by

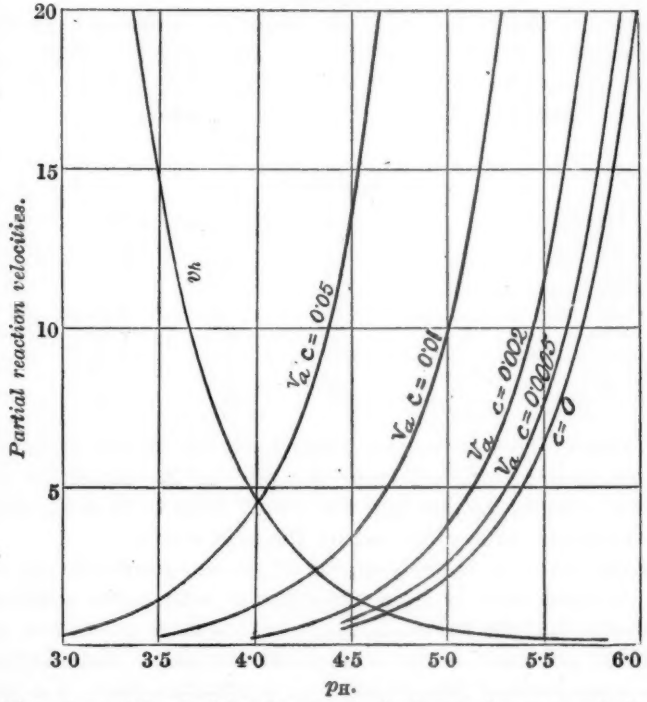
$$v_h = k_h \cdot 10^{-p_H} \text{ and } v_a = (k_aKc + k_{OH}K_w)10^{p_H}$$

The curve for v_h and a group of v_a curves for acetic acid concentrations ranging from $c = 0$ to $c = 0{\cdot}05N$ are shown in the diagram and it need only be pointed out that the p_H values of the points of intersection of the v_h curve with the several v_a curves are identical with the *M.V.* points of the corresponding catenaries under the conditions which are here postulated.

In regard to the compound catenaries, it should be added that these conform to the requirements of the general catenary in exactly the same way as the simple catenaries. The applicability of the general catalytic catenary is thus further extended to include ionic catalytic effects in which the contribution of the negative ions is shared by anions derived respectively from the solvent and from the acid–salt mixture present in the solution.

The bearing of the above results on the use of buffer mixtures for the study of the velocity of hydrolytic reactions is obvious. The minimum velocities observed under such conditions are larger, and the p_H values smaller than those which would correspond with the *M.V.* point characteristic of the undisturbed action of the hydrogen and hydroxyl ions. In this connexion, it may be noted that since the buffer acid is weak (k_m negligible in comparison with k_h), equations (10) and (11) give $u_i/[H^+]_i = 2k_h$, which is identical with

FIG. 1.



Plot of partial velocities due to the hydrogen ion (v_h) and the acetate + hydroxyl ions (v_a) against p_H.

equation (3). It must be remembered, however, that the ionic reaction velocity u_i is not directly measurable. On the assumption that the undissociated water molecules have no measurable activity, the ionic reaction velocity is derived from $u_i = v_i - k_m c$, which requires a knowledge of the catalytic activity of the undissociated buffer acid.

In the circumstances outlined above, it is apparent that the observations made by Karlsson (*Z. anorg. Chem.*, 1921, **119**, 69; 1925, **145**, 1) and Bolin (*ibid.*, 1925, **143**, 201) do not yield either

$(p_H)_i$ values or minimum reaction velocities which can be utilised directly for the derivation of k_h or k_{OH} with any approach to accuracy.

Notwithstanding the approximate character of the $(p_H)_i$ values recorded by Karlsson and Bolin, their data serve to show that the ratio k_{OH}/k_h varies enormously with the nature of the catalysed reaction. The values obtained from the logarithmic equivalent of equation (5), *viz.*,

$$\log k_{OH}/k_h = -\log K_w - 2(p_H)_i,$$

are shown in the fifth column of Table II. Column 1 shows the hydrolyte, col. 2 the temperature of the velocity measurements, col. 3 the ionisation product of water at this temperature, and col. 4 the $(p_H)_i$ values recorded by the above observers.

TABLE II.

Hydrolyte.	Temp.	$K_w \times 10^{14}$.	$(p_H)_i$.	k_{OH}/k_h.
Methyl acetate	25°	1·0	5·15	5,000
Ethyl acetate	25	1·0	5·36	1,900
Glycerol monoacetate	25	1·0	5·0	10,000
Ethyl chloroacetate	20	0·8	4·8	32,000
Ethyl formate	20	0·8	4·65	63,000
Ethyl aminoacetate	20	0·8	3·5	12×10^6
Acetanilide	40	4·0	5·80	63
Benzamide	80	25	6·2	1·6

The value of $(p_H)_i$ given for methyl acetate is that derived by Karlsson (*loc. cit.*, p. 31) from the plot of the logarithm of the observed velocity against p_H; this would seem to be more accurate than the lower value indicated by the v–p_H curve.

For the first five hydrolytes, for which the recorded $(p_H)_i$ values were obtained directly from experiments with buffer solutions, it is probable that the values of k_{OH}/k_h are too large on account of the disturbing influence of the buffer acid and salt. Some indication of the magnitude of this disturbance is obtained when it is pointed out that the correct value of k_{OH}/k_h for ethyl acetate is about 1000. The $(p_H)_i$ values recorded by Bolin for acetanilide and benzamide were derived on the assumption that the acid and alkaline branches of the v–p_H curve are symmetrical with respect to the point of minimum reaction velocity. This empirical assumption is entirely in agreement with the theoretical conclusion reached by Dawson and Dean (J., 1926, 2872) that the p_H value of the *M.V.* point is the arithmetic mean of the p_H values for pairs of solutions of the series cHA + xMA which have the same catalytic power.

The application of the isocatalytic method to the systematic determination of the ratio k_{OH}/k_h by the rational use of buffer

solutions should make it possible to extend the number of reactions for which this ratio can be derived and thus provide material for the investigation of the question of the mode of action of the hydrogen and hydroxyl ions as catalytic agents in so-called hydrolytic reactions.

Summary.

It is shown that the velocity coefficients k_h and k_{OH} can be derived from the isocatalytic data v_i and $[H^+]_i$.

Approximate values of v_i and $[H^+]_i$ may be obtained by the use of buffer solutions, but the experimental data, which indicate that k_{OH}/k_h varies with the hydrolyte between very wide limits, must be corrected for the catalytic effects which are produced by constituents of the buffer solutions other than the hydrogen and hydroxyl ions.

The curves obtained by plotting the reaction velocity against the p_H value of a series of buffer solutions, in which the concentration of the acid is constant, are catenary in type. These catenary curves are compound in character in that the anionic catalytic effect is shared by the hydroxyl ion and by the anion of the acid in the buffer mixture.

The compound catenaries form a continuous series limited on the one hand by the H^+–OH^- catenary, and on the other by the simple H^+–A^- catenaries corresponding with the mixtures cHA + xMA.

The compound catenaries conform to the requirements of the general catalytic catenary, the application of which is thus extended to include anionic catalytic effects which are shared by the hydroxyl ion with other acid anions.

THE UNIVERSITY, LEEDS. [*Received, March 17th*, 1927.]

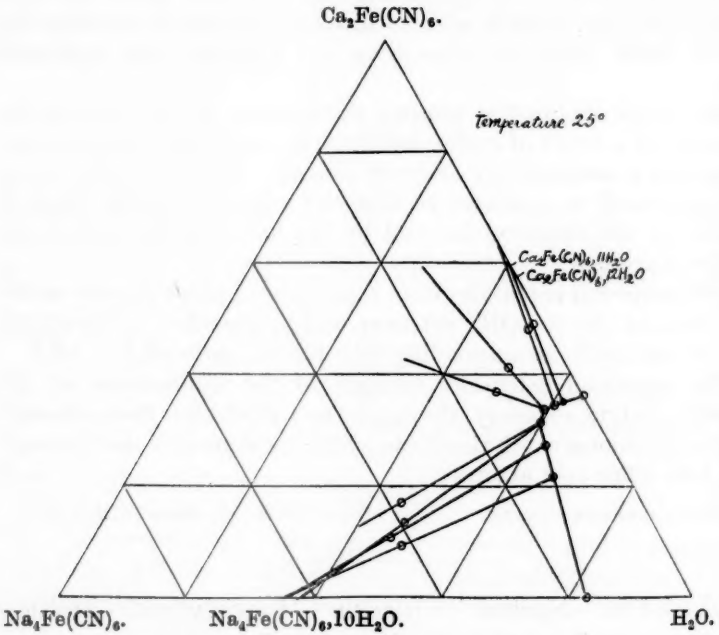
CLX.—*The System Calcium Ferrocyanide–Sodium Ferrocyanide–Water. Part II.*

By MONICA FARROW.

THE solubility equilibria of the systems calcium ferrocyanide–water and sodium ferrocyanide–water were described by the author in a previous paper (J., 1926, 49), in which it was shown that $Na_4Fe(CN)_6,10H_2O$ undergoes transformation into a less hydrated form at 81·5°. The present paper deals with the three-component system calcium ferrocyanide–sodium ferrocyanide–water, which was investigated with the view of determining by the "Rest" method the formula of the sodium salt which is stable at higher temperatures. This object was not attained, as the two ferro-

cyanides gave the double salt $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$. This salt, which is of the same type as the well-known double salts of calcium and potassium or ammonium ferrocyanides, has been obtained by Wyrouboff (*Ann. Chim.*, 1870, **21**, 283) by crystallisation from solutions of the mixed components, but the product so prepared was evidently not pure, since Wyrouboff's analyses led him to formulate it as $CaNa_3Fe(CN)_6$. Crystals of the double salt now obtained have been examined by Dr. T. V. Barker, who finds that their crystallographic properties agree with those stated by Wyrouboff.

FIG. 1.



Nevertheless, the system was of some interest and was investigated in detail. The range of the solubility determinations of the calcium salt was extended from the cryohydrate to 90°, and it was found, like the sodium salt, to suffer transformation to a lower state of hydration.

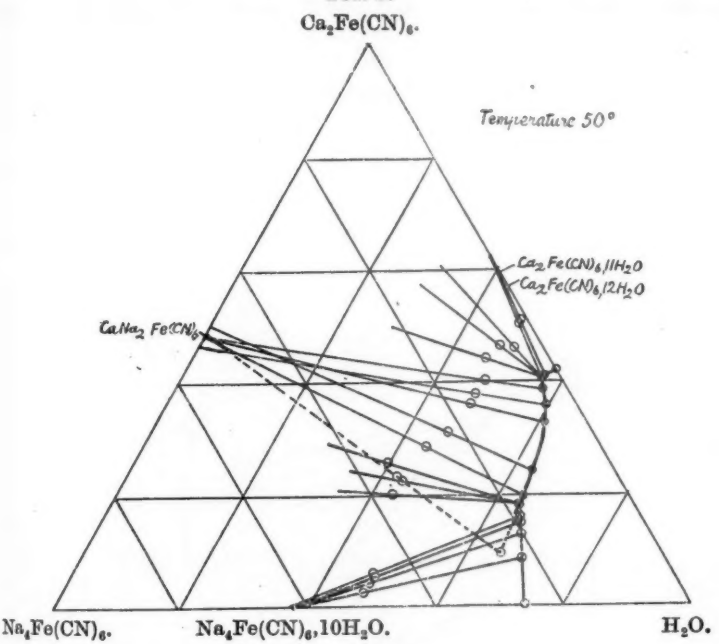
EXPERIMENTAL.

System Calcium Ferrocyanide–Water.

Determination of the solubility of the pure calcium salt at 90° gave 44·2 g. of anhydrous salt per 100 g. of solution, a value almost identical with that obtained at 65°, *viz.*, 44·4 g. In the course

of the former experiments five independent determinations of the solubility at 80° were made, giving a mean value of 44·0. These experiments clearly indicate a change of the ordinary hydrate into a form which is stable at higher temperatures and the solubility of which is practically independent of temperature. From cooling curves it appears that the lower limit of stability of the new form is 59·7°. The complete solubility curve of calcium ferrocyanide is

FIG. 2.



now given from −11·6° to 90° as g. of anhydrous salt in 100 g. of solution.

Temp. ...	−10·1°	24·9°	34·9°	49·8°	59·7°	64·7°	79·6° & 90°
Conc. ...	30·45	36·44	39·22	42·04	44·20	44·44	44·37

System Calcium Ferrocyanide–Sodium Ferrocyanide–Water.

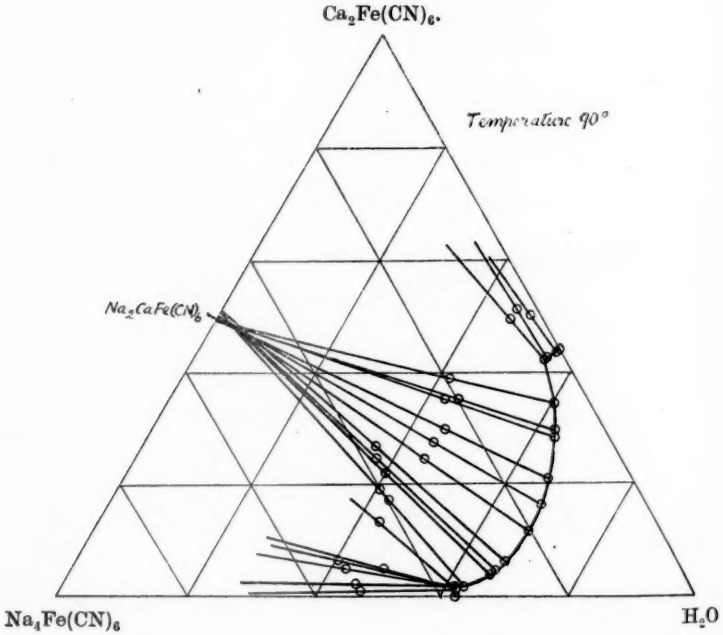
The composition of the solutions and of the wet solids in equilibrium with them were determined by the methods previously described in detail (*loc. cit.*), *viz.*, the total ferrocyanide by permanganate, and the calcium volumetrically by the oxalate method. The withdrawal of solutions by means of the weight pipette previously described enabled density as well as solubility determinations to be made. The experiments were carried out at 25°, 50°, and 90°,

and the results obtained are in the following tables, and represented in Figs. 1, 2, and 3. The values represent weights of anhydrous salt per 100 g. of solution in columns 2 and 3, and per 100 g. of wet solid in columns 5 and 6. The triple-point values are starred. (*M* represents metastable state.)

Determination of Invariant Points.

1. The transition point of pure calcium ferrocyanide was found by means of cooling curves to be 59·7°, and in the presence of the

FIG. 3.



solid double salt to be 58·2°. The solubility of the pure salt was 44·2 g. in 100 g. of solution.

2. The transition point of pure sodium ferrocyanide, determined by the same method, was 81·5°, and when the solid double salt was present, it was 81·16°. The composition of the solution at the former temperature was 37·5 g. of $Ca_2Fe(CN)_6$ in 100 g. of solution, and at the latter 3·14 g. of $Ca_2Fe(CN)_6$, 34·74 g. of $Na_4Fe(CN)_6$, and 62·14 g. of water.

3. The melting point of the calcium ferrocyanide cryohydrate was found to be −10·1° and its composition was 30·45 g. of anhydrous salt per 100 g. of solution, which had *d* 1·198.

	Solutions.			Solids.		
D.	$Ca_2Fe(CN)_6$.	$Na_4Fe(CN)_6$.	H_2O.	$Ca_2Fe(CN)_6$.	$Na_4Fe(CN)_6$.	H_2O.
At 25°.						
1·356	37·16	—	62·84	—	—	—
1·369	35·27	3·67	61·05	49·00	1·23	49·76
1·373	35·10	4·79	60·11	48·71	3·01	48·33
* 1·381	33·24	7·55	59·21	42·22	9·55	48·24
—	33·40	7·33	59·27	37·76	14·66	47·60
* —	31·30	8·46	60·24	17·31	37·37	45·27
—	31·60	8·75	59·65	13·97	38·25	47·71
1·344	28·02	9·64	62·34	11·40	42·26	46·41
—	22·22	11·50	66·27	9·88	41·76	48·38
1·130	—	17·04	82·96	—	—	—
At 50°.						
1·392	42·20	—	58·00	—	—	—
—	40·71	2·53	56·78	50·51	1·42	48·08
—	40·51	2·91	56·58	49·30	1·83	49·90
* 1·436	39·95	2·65	57·38	46·46	6·54	46·98
1·438	40·10	2·91	57·00	43·98	9·85	46·17
—	38·70	3·30	57·94	40·10	11·31	48·61
—	36·07	4·73	59·20	37·79	14·65	47·59
1·363	33·08	6·50	60·44	36·63	15·90	47·46
1·332	24·40	12·99	62·61	32·07	23·11	44·81
1·314	20·05	16·24	63·71	29·45	27·73	42·83
1·308	17·28	18·49	64·24	26·32	31·20	42·46
* 1·311	18·13	18·00	63·87	23·39	34·04	42·51
1·310	17·93	18·44	63·62	20·58	37·22	42·22
M 1·280	9·53	25·25	65·26	23·88	34·18	41·91
1·300	16·26	18·65	65·10	6·09	47·17	46·79
1·296	15·57	19·37	65·52	5·71	47·38	46·96
1·281	13·18	20·10	66·74	4·59	48·41	47·01
1·255	9·13	22·11	68·76	3·01	49·61	47·38
1·200	—	26·20	73·80	—	—	—
At 90°.						
1·401	44·40	—	55·60	—	—	—
1·400	43·96	0·34	55·70	50·35	1·71	47·88
1·396	42·74	2·77	54·50	50·81	2·99	46·20
* —	42·42	3·12	54·44	49·16	4·47	46·37
1·335	34·74	5·02	60·27	39·05	19·22	41·73
1·313	30·17	7·43	62·39	35·52	19·90	44·57
1·307	29·09	8·08	62·82	35·66	22·55	41·80
1·307	21·34	13·09	65·56	30·27	25·50	44·26
1·249	16·64	16·28	67·07	28·32	28·21	43·56
—	14·88	18·18	66·94	27·40	29·73	42·86
1·238	11·99	20·29	67·71	25·50	31·15	43·36
1·238	11·44	20·49	68·13	23·56	29·52	46·90
1·242	6·54	26·83	66·61	25·94	35·85	38·20
1·240	6·49	26·72	66·67	29·03	37·10	33·89
1·252	4·88	29·48	65·53	25·60	37·79	36·62
1·256	3·83	31·36	64·97	23·33	39·02	37·64
1·266	2·89	33·55	63·59	21·47	38·35	40·19
1·279	2·20	35·36	62·46	19·08	40·36	40·56
1·284	2·21	35·77	62·02	17·45	39·81	42·73
1·302	1·46	38·97	59·58	13·97	43·54	42·47
* 1·285	1·88	37·04	61·05	6·87	53·15	39·95
1·285	1·81	36·81	61·38	5·63	47·55	46·81
1·288	1·72	36·97	61·31	2·41	52·52	45·03
1·288	1·37	37·35	38·73	1·30	54·55	44·13
1·290	—	38·00	62·00	—	—	—

4. The cryohydric temperature of sodium ferrocyanide was estimated as −1·40° and the concentration as 6·81 g. in 100 g. of solution. The density, by extrapolation, is 1·130.

5. The cryohydric temperature for the three-component system was −11·6°, and the concentrations were $Ca_2Fe(CN)_6$, 28·9; $Na_4Fe(CN)_6$, 3·587; H_2O, 67·51%.

Discussion.

At all three temperatures investigated, the double salt is stable, and the range of stability increases markedly with rise in temperature. The range of solutions in equilibrium with the double salt $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$ moves over very much towards the calcium side at lower temperatures. The solubility curve for the double salt is continued into the metastable region at 50° as shown in the diagram.

The values obtained at 25° and 50° confirm the accepted formula of the sodium salt as $Na_4Fe(CN)_6,10H_2O$, and provide additional evidence that the formula of the calcium salt is $Ca_2Fe(CN)_6,11H_2O$ and not $Ca_2Fe(CN)_6,12H_2O$, as might be expected. The evidence at 90° is less satisfactory, as the range of solutions with which the simple salt is in equilibrium is in both cases very limited. The values obtained are sufficient to show that at this temperature the stable forms of the two salts are less highly hydrated than at the lower temperatures, but precise formulation must await the investigation of other systems. Both at 90° and at 50° the tie-lines clearly indicate a formula $Ca_2Fe(CN)_6,Na_4Fe(CN)_6$ for the double salt. At 50°, both the single salts are highly hydrated; the tendency of the double salt to combine with water is thus markedly less than that of the single salts. In its temperature coefficient of solubility it also diverges considerably from the behaviour of the hydrated components, for its solubility clearly falls with increase in temperature. This fact is also probably connected with the absence of hydration, since the dehydrated forms of the single salts have no appreciable temperature coefficient of solubility.

The author would like to express her thanks to Mr. M. P. Applebey for much valuable advice and criticism during the course of the work, and to Dr. T. V. Barker, Reader in Crystallography, for the crystallographic measurements of the calcium–sodium double salt.

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CLXI.—*The Interaction of Alkali Sulphites with some Halogeno-compounds, and the Optical Resolution of α-Phenylpropanesulphonic Acid.*

By ERIC BERTRAM EVANS, ERNEST EDWARD MABBOTT, and EUSTACE EBENEZER TURNER.

THE original object of this work was to determine whether the interaction of sodium sulphite and asymmetric halogen compounds of the type CHRR'X would afford a practicable method for the preparation of some optically resolvable sulphonic acids required for another investigation. We have, however, not been concerned with the sulpho-carboxylic acids, which have been simultaneously investigated by Backer and Burgers (see, for example, J., 1925, **127**, 233).

Cohen and Clutterbuck (J., 1923, **123**, 2507) stated that β-phenylethyl chloride was converted by boiling aqueous sodium sulphite into styrene, with evolution of sulphur dioxide. We find, however, that the chloride is converted under these conditions into a mixture of *sodium β-phenylethanesulphonate*, $CH_2Ph{\cdot}CH_2{\cdot}SO_3Na$ (65% yield), and β-phenylethyl alcohol, no appreciable evolution of sulphur dioxide occurring. Sodium or potassium sulphite converts β-phenylethyl bromide even more rapidly and completely into sulphonate.

β-Phenylethanesulphonyl chloride and the corresponding *amide* and *anilide* are readily obtainable from the sodium sulphonate. The isolation of the amide makes it possible to cite the series $Ph{\cdot}[CH_2]_x{\cdot}SO_2{\cdot}NH_2$ as another in which there is an alternation in melting point (compare Roberts, Turner, and Bury, J., 1926, 1443): for $x = 0$, 1, 2, and 3, the m. p.'s are respectively 153°, 105°, 119°, and 35°.

Similarly, α-phenylethyl chloride (bromide) reacts with boiling aqueous sodium sulphite to give *sodium α-phenylethanesulphonate*, $CHPhMe{\cdot}SO_3Na$ (yield, 43—45%). Considerable evolution of sulphur dioxide occurs and some styrene is formed.

Fittig and Kiesow (*Annalen*, 1870, **156**, 246) and, later, Anschütz (*ibid.*, 1886, **235**, 329) concluded that chlorination of boiling ethylbenzene afforded mainly β-phenylethyl chloride, whilst Schramm (*Monatsh.*, 1887, **8**, 102; *Ber.*, 1893, **26**, 1706) obtained a mixture of the α- and β-chlorides. We find that pure ethylbenzene, prepared from acetophenone (Clemmensen, *Ber.*, 1913, **46**, 1840), chlorinates readily in diffused daylight to give (corresponding to monochlorination) a mixture of α- and β-phenylethyl chlorides with higher-boiling material (αβ-dichlorophenylethane, etc.), increased illumination appearing to augment the proportion of α-chloride.

When the contained α- and β-chloride mixture is boiled with aqueous sodium sulphite, it gives rise to appreciable quantities of sulphur dioxide and styrene, but at the same time to a mixture of the corresponding sodium sulphonates.

Dimethylaniline is indifferent towards β-phenylethyl chloride, but combines with the α-chloride to give the crystalline *phenyl-α-phenylethyldimethylammonium chloride*, $CHPhMe{\cdot}NPhMe_2Cl$. When a mixture, with dimethylaniline, of the above purified chlorination mixture was kept for several months, it deposited no solid, a fact which shows that the mixture was predominatingly β-chloride.

The chlorination of ethylbenzene probably gives, as the first product, mainly β-phenylethyl chloride, but the decomposition of this substance, during the chlorination process, produces styrene, which combines either with hydrogen chloride or with chlorine :

$$CH_2Ph{\cdot}CH_3 \longrightarrow CH_2Ph{\cdot}CH_2Cl \longrightarrow CHPh{:}CH_2 \begin{matrix} \nearrow CHPhCl{\cdot}CH_3 \\ \searrow CHPhCl{\cdot}CH_2Cl \end{matrix}$$

When *strychnine* dl-α-*phenylethanesulphonate* was crystallised from water, *strychnine* l-α-*phenylethanesulphonate* separated first.

As considerable quantities of phenylmethylcarbinol were required for this work, we re-examined the reduction of acetophenone, using sodium and moist ether–toluene. The main product was, however, αβ-diphenyl-αβ-dimethylethane-αβ-diol (acetophenone pinacol). This is therefore, apparently, the best way of obtaining this substance, since in 1917 (*J. Amer. Chem. Soc.*, **39**, 291) Johlin, who investigated various methods for its preparation, including the reduction of acetophenone by other processes, concluded that it was then most conveniently prepared from magnesium methyl iodide and benzil.

α-Phenylpropyl bromide also reacted with boiling aqueous sodium sulphite, but only about 10% was converted into *sodium α-phenylpropanesulphonate*, $CHPhEt{\cdot}SO_3Na$. Prolonged shaking of the reactants at the ordinary temperature, however, gave a 30% yield. When an aqueous solution of *α-phenylpropanesulphonic acid* was treated with half an equivalent of strychnine, it afforded the sparingly soluble *strychnine* d-α-*phenylpropanesulphonate* with $[\alpha]_D^{26°}$ — 23·7°; the mother-liquor gave, with cinchonine, the l-α-*phenylpropanesulphonate* of the latter base, having $[\alpha]_D^{25°}$ + 104·9°. From the two alkaloidal salts were obtained the two *sodium* salts, with $[\alpha]_D^{25°}$ + 5·2° and — 5·2°, respectively.

α-*Phenylbutyl bromide* reacted slowly with aqueous sodium sulphite at the ordinary temperature to give a little *sodium α-phenylbutane-*

sulphonate, $CHPhPr^{\alpha}\cdot SO_3Na$, the majority of the bromo-compound, however, being converted into α-phenyl-Δ^{α}-butene.

In other experiments designed to provide α-phenylbutanesulphonic acid, magnesium α-phenylbutyl bromide was found to react with sulphur dioxide to give, instead of the desired sulphinic acid, *di-α-phenylbutyl sulphide* $(PhPr^{\alpha}CH)_2S$ (compare Rosenheim and Singer, *Ber.*, 1904, **37**, 2152; Oddo, *Gazzetta*, 1911, **41**, 11).

The effect upon the conversion of α-phenylethyl halides into sodium sulphonates, of negative substituents in the benzene ring was also tested. 2 : 4-Dichloroiodobenzene (Ullmann, *Annalen*, 1904, **332**, 38) combined with magnesium to give magnesium 2 : 4-dichlorophenyl iodide, and this reacted with acetaldehyde to give 2 : 4-*dichlorophenylmethylcarbinol*. No difficulty was experienced in converting this substance into the corresponding *bromide*, but when the latter was treated with boiling aqueous sodium sulphite, it was almost quantitatively converted into the carbinol. This result is somewhat similar to that observed by Wedekind and Schenk (*Ber.*, 1911, **44**, 198) with diphenylhalogenomethanes, when the corresponding ether was formed as the only product. No 2 : 4-dichlorostyrene was produced in the above reaction, this fact and the above formation of carbinol being apparently due to the negative effect of the ortho-para chlorine atoms. Again, α-2 : 4-dichlorophenylethyl bromide is devoid of lachrymatory properties, unlike α-phenylethyl bromide itself.

β-Bromobutane, readily obtainable from methyl ethyl ketone (Bentley, J., 1895, **67**, 264; Norris, Green, and Johnson, *Amer. Chem. J.*, 1901, **26**, 293), reacted at a convenient rate with warm aqueous sodium sulphite to give over half the calculated quantity of *sodium α-methylpropanesulphonate*, $CHMeEt\cdot SO_3Na$. *Strychnine* d-α-*methylpropanesulphonate* is less soluble in water than its diastereoisomeride. No other alkaloidal salt could be obtained crystalline.

Experimental.

Sodium β-Phenylethanesulphonate.—(a) *From β-phenylethyl chloride.* A mixture of 20 g. of the chloride with a saturated aqueous solution of 40 g. of sodium sulphite heptahydrate was heated to boiling for 20 hours; 4 g. of oil, identified as β-phenylethyl alcohol, remained undissolved. No sulphur dioxide evolution was observed during the process. The cooled reaction mixture deposited a mass of crystals which, after crystallisation from water, gave white plates of *sodium β-phenylethanesulphonate* (yield, 65%) (Found : Na, 11·1. $C_8H_9O_3SNa$ requires Na, 11·1%). (b) *From β-phenylethyl bromide.* A mixture of 37 g. of the bromide and a saturated solution of 55 g. of sodium sulphite was boiled under reflux. Crystals began to form in the

boiling solution after 2·5 hours, and in 3 hours the bromide had disappeared. On cooling, the liquid set to a crystalline mass, which was filtered off. The solid was crystallised from water, a 90% yield of the sodium sulphonate being obtained (Found : Na, 11·2%).

The *potassium* salt was obtained similarly, and separated from water in white plates (yield, 90%) (Found : K, 17·3. $C_8H_9O_3SK$ requires K, 17·4%). The *barium* salt was precipitated when concentrated solutions of barium chloride and of the above sodium salt were mixed. Recrystallised from water, it formed small leaflets (Found : Ba, 27·2. $C_{16}H_{18}O_6S_2Ba$ requires Ba, 27·0%).

β-*Phenylethanesulphonic acid*, obtained from the barium salt and an equivalent of sulphuric acid, crystallised from very concentrated solutions in small, deliquescent leaflets, m. p. 91°. After being left in contact with porous porcelain for a short time in a dry atmosphere, it was found to contain 5 mols. of water of crystallisation.

β-*Phenylethanesulphonyl Chloride*.—The sodium salt reacted normally with phosphorus pentachloride to give the *sulphonyl chloride*, which crystallised from light petroleum in white, silky needles, m. p. 34° (Found : Cl, 17·6. $C_8H_9O_2ClS$ requires Cl, 17·4%).

β-*Phenylethanesulphonamide* was obtained by passing dry ammonia into a well-cooled ethereal solution of the chloride. It separated from water in white plates, m. p. 119° (Found : N, 7·3. $C_8H_{11}O_2NS$ requires N, 7·6%). The chloride reacted readily in ethereal solution with aniline, giving the *anilide*, which crystallised from aqueous alcohol in white needles, m. p. 77° (Found : N, 5·2. $C_{14}H_{15}O_2NS$ requires N, 5·4%).

Sodium α-*Phenylethanesulphonate*.—A mixture of 40 g. of α-phenylethyl bromide and a saturated solution of 60 g. of sodium sulphite was boiled under reflux. A brisk evolution of sulphur dioxide occurred, and the layer of organic liquid, at first at the bottom, rose to the top. When, after 6 hours' boiling, no more sulphur dioxide was evolved, the liquid was cooled. The top layer consisted of styrene (10 g.), and the aqueous layer, after being evaporated to about two-thirds of its original bulk, deposited white plates on cooling. These were crystallised from water (yield, 45%) (Found : Na, 11·1. $C_8H_9O_3SNa$ requires Na, 11·1%).

When 100 g. of α-phenylethyl bromide was used for this preparation, only 10 g. of sulphonate were obtained; the use of small quantities is therefore to be recommended.

With α-phenylethyl chloride (30 g.) instead of the bromide, the reaction was complete in 9 hours, and a 43% yield of sodium salt was obtained.

Barium α-*phenylethanesulphonate* crystallised in long needles when a solution containing the sodium salt and the calculated

quantity of barium chloride was cooled (Found: Ba, 27·3. $C_{16}H_{18}O_6S_2Ba$ requires Ba, 27·0%). The *potassium* salt, obtained from the barium salt and potassium sulphate, crystallised from water in plates (Found: K, 17·5. $C_8H_9O_3SK$ requires K, 17·4%).

α-Phenylethanesulphonyl chloride, formed from the sodium salt in the usual manner, separated from alcohol in small, white needles, m. p. 79° (Found: Cl, 17·5. $C_8H_9O_2ClS$ requires Cl, 17·4%).

Chlorination of Ethylbenzene.—When chlorine was passed into boiling ethylbenzene in bright sunlight (Sydney, N.S.W.), chlorination was very rapid and gave a mixture of polychloro-derivatives. Dry chlorine was passed for 4 hours into 30·7 g. of boiling ethylbenzene in bright sunlight (London) until an increase of 9 g. in weight occurred. The product separated when distilled into three fractions: (1) b. p. up to 82°/15 mm., 2 g.; (2) b. p. 82—100°/15 mm., 16 g.; and (3) b. p. 100—125°/15 mm., 12 g. Fraction (2) was boiled with sodium sulphite solution. Sulphur dioxide was evolved, and after 8 hours the solution was cooled; crystals of the sulphonate mixture then separated and 2 g. of styrene were isolated. Fraction (3) was rich in αβ-dichlorophenylethane.

A second chlorination of 43 g. of ethylbenzene, carried out on a very dull day, lasted 9 hours. The product was separated into 3 fractions: (1) b. p. up to 82°/15 mm., 3 g.; (2) b. p. 82—102°/15 mm., 20 g.; and (3) b. p. 102—120°/15 mm., 20 g. Fraction (2), the greater portion of which distilled at 90—100°/15 mm., was only slightly lachrymatory and was evidently mainly β-phenylethyl chloride; for, when it was heated with sodium sulphite, it gave rise to very little sulphur dioxide and styrene, and a good yield of sulphonate.

Equimolecular mixtures, with dimethylaniline, of α- and β-phenylethyl chlorides and fraction (2) of the last chlorination were allowed to remain at the ordinary temperature for 5 months. The mixture containing the α-chloride became almost solid. The product was left in contact with porous porcelain in a dry atmosphere, and then became a colourless, crystalline mass of *phenyl-α-phenylethyldimethylammonium chloride*, m. p. 95° (Found: Cl, 13·6. $C_{16}H_{20}NCl$ requires Cl, 13·6%). The other two mixtures deposited no solid.

Strychnine dl-*α-Phenylethanesulphonate.*—To a boiling aqueous solution of barium α-phenylethanesulphonate (21·99 g.) was added a boiling solution of 29 g. of strychnine in the equivalent quantity of *N*-sulphuric acid. The barium sulphate was collected, and the filtrate was evaporated almost to dryness. The solid so obtained was analysed (Found: N, 5·6. $C_{21}H_{22}O_2N_2,C_8H_{10}O_3S$ requires N, 5·4%).

Fractional crystallisation of this racemate gave *strychnine* l-α-*phenylethanesulphonate* as the less soluble salt. A 1·874% solution in 50% aqueous alcohol had $\alpha_D^{18°}$ — 0·81° (2-dcm. tube), whence $[\alpha]_D^{18°}$ — 20·5°.

Similarly, when a hot solution of 4·62 g. of sodium α-phenylethanesulphonate was treated with a hot solution of 3·71 g. of strychnine (dissolved in an equivalent of *N*-sulphuric acid), and the solution allowed to cool, pure strychnine *l*-sulphonate separated, having $[\alpha]_D^{18°}$ — 20·5°.

Potassium l-α-*phenylethanesulphonate* was obtained by treating the strychnine salt with potassium carbonate. A 1·90% solution in water had $\alpha_D^{18°}$ — 0·45° (l = 2 dcm.), whence $[\alpha]_D^{18°}$ — 11·8°.

Systematic treatment of the mother-liquors from the strychnine *l*-sulphonate did not afford a pure *d*-sulphonate.

Brucine dl-α-*phenylethanesulphonate* was obtained crystalline only after a great deal of preliminary treatment. It was very soluble in water, alcohol, ether, carbon tetrachloride, and acetone, though sparingly soluble in benzene, and could not be caused to crystallise systematically (Found: N, 5·1. $C_{23}H_{26}O_4N_2,C_8H_{10}O_3S$ requires N, 4·8%). *Cinchonidine* dl-α-*phenylethanesulphonate* was even more difficult to obtain crystalline, and could not be fractionally crystallised, being very soluble in most solvents (Found: N, 4·4. $C_{27}H_{32}O_4N_2,C_8H_{10}O_3S$ requires N, 4·2%).

Preparation of αβ-*Diphenyl*-αβ-*dimethylethane*-αβ-*diol*.—A solution of acetophenone (60 g.) in moist ether (150 c.c.) was slowly added to 46 g. of powdered sodium covered with 100 g. of toluene. Water was then added gradually. After a time, the whole became practically solid. Water was added until the solid redissolved, the ether–toluene layer then being removed, washed, dried and distilled, until the residue was at 150°. On cooling, it solidified, and after several crystallisations from alcohol and benzene melted at 121° (Found: *M*, cryoscopic in benzene, 232, 251. Calc.: *M*, 242).

Preparation of 2 : 4-*Dichlorophenylmethylcarbinol*.—2 : 4-Dichloroiodobenzene (68 g.; b. p. 255—257° [Ullmann, *Annalen*, 1904, **332**, 38, gives 262—263°]; obtained from 2 : 4-dichloroaniline), when dissolved in ether, combined readily with magnesium (6 g.) in presence of a little iodine. The solution was treated gradually with an ethereal solution of 16 g. of acetaldehyde. The mixture was left over-night and then treated with ice and dilute hydrochloric acid, and the ethereal solution was washed with aqueous sodium hydrogen carbonate, with aqueous sodium hydrogen sulphite, and with sodium hydrogen carbonate. It was then dried; the carbinol, by distillation under diminished pressure, was obtained as a pale

yellow liquid, b. p. 145°/20 mm., or 154—155°/29 mm. (yield 67%) (Found : Cl, 38·5. $C_8H_8OCl_2$ requires Cl, 37·2%).

α-2 : 4-*Dichlorophenylethyl Bromide.*—Hydrogen bromide was passed into the carbinol for 4 hours, and the product was treated with dilute sodium carbonate solution, then with water, and finally distilled under diminished pressure. The bromide was obtained as a mobile, colourless liquid, b. p. 154°/37 mm., with hardly any odour or lachrymatory properties (Found : AgCl + AgBr, 0·3350. $C_8H_7Cl_2Br$ requires AgCl + AgBr, 0·3418).

Action of Sodium Sulphite on α-2 : 4-*Dichlorophenylethyl Bromide.*—The bromide (10 g.) was heated with a solution of sodium sulphite for 30 hours; 7 g. of the carbinol (calc., 7·5 g.) were then obtained, b. p. 154°/29 mm.

Preparation of 3 : 5-*Dichlorobromobenzene.*—When 2 : 4-dichloroacetanilide was brominated in glacial acetic acid solution, it was converted into slightly more than its own weight of 2 : 4-dichloro-6-bromoaniline, m. p. 81°, the acetyl group being eliminated in the process. Treatment of the base with sodium nitrite, alcohol, benzene and concentrated sulphuric acid in the usual manner gave a 38% yield of 3 : 5-dichlorobromobenzene. This substance, after several crystallisations from alcohol, melted at 74°, although Hartley (J., 1901, **79**, 1293) gives 77·5°, and Hantzsch (*Ber.*, 1897, **30**, 2351) gives 82—84°. It reacted with magnesium which had previously been activated with methyl iodide.

Sodium α-*Phenylpropanesulphonate.*—α-Phenylpropyl bromide (15 g.) was heated in the usual manner with sodium sulphite solution. Propenylbenzene was the main product, only 2 g. of impure sulphonate being obtained. Ammonium sulphite gave similar results.

The bromide (90 g.) was shaken vigorously for 120 hours with a solution of 120 g. of sodium sulphite heptahydrate in 240 c.c. of water. After several hours' shaking, crystals began to separate, and when no further change was apparent the solid was collected and the oily layer separated (35 g.). The solid was freed from bromide and sulphite by systematic crystallisation from water, and ultimately gave 30 g. (30% yield) of pure sodium α-phenylpropanesulphonate, very soluble in water, but almost insoluble in alcohol (Found : Na, 10·4. $C_9H_{11}O_3SNa$ requires Na, 10·4%).

In a second experiment, 60 g. of bromide gave 21 g. (32% yield) of sulphonate and 23 g. of oil. From the density of the latter it was estimated that it contained about 6 g. of unchanged bromide and 17 g. of propenylbenzene. This indicates that, in the above experiment, about 50% of the bromide underwent loss of hydrogen bromide.

α-*Phenylpropanesulphonic Acid.*—Addition of barium chloride

solution to one of the sodium sulphonate caused the precipitation of a mixture of salts which could not be separated. The free acid was therefore prepared as follows : A hot concentrated solution of the sodium salt was treated with an excess of concentrated hydrochloric acid, and the sodium chloride removed. The liquid was evaporated, and the whole process repeated four times; on final evaporation, the sulphonic acid was obtained as a deliquescent, gummy solid which partly crystallised on desiccation for some weeks, but could not be recrystallised from a solvent.

α-Phenylpropanesulphonyl chloride was obtained from the sodium salt and phosphorus pentachloride as a colourless, heavy liquid, b. p. 175°/20 mm. (Found : Cl, 15·9. $C_9H_{11}O_2ClS$ requires Cl, 16·3%). The corresponding *amide* and *anilide* could not be caused to crystallise.

Resolution of dl-*α-Phenylpropanesulphonic Acid.*—Finely powdered strychnine (4·15 g.) was allowed to dissolve in a hot aqueous solution of 5 g. (2 equivs.) of the sulphonic acid. On cooling, the strychnine salt separated, and this, after being recrystallised three times from water, weighed 3 g. (0·1644 g. was equivalent to 3·00 c.c. of 0·1*N*-sodium hydroxide. $C_{21}H_{22}O_2N_2,C_9H_{12}O_3S$ requires 3·10 c.c.). The salt had $[\alpha]_D^{28°}$ — 23·7° in aqueous alcohol (water, 1 vol.; alcohol, 2 vols.), and was unaffected by further recrystallisation.

To the heated mother-liquor remaining after removal of the strychnine salt, 0·5 equivalent (3·7 g.) of cinchonine was added. When further dissolution ceased, a little cinchonine was filtered off, and the filtrate was cooled. The precipitated solid was recrystallised thrice from water; 2·6 g. of *cinchonine* salt were then obtained (0·1184 g. was equivalent to 2·20 c.c. of 0·1*N*-sodium hydroxide. $C_{20}H_{21}O_4N,C_9H_{12}O_3S$ requires 2·40 c.c.). The salt had $[\alpha]_D^{25°}$ + 104·9° in aqueous alcohol, and was not affected by further crystallisation.

The alkaloidal salts were converted into the *sodium* salts by treatment with the calculated quantity of sodium hydrogen carbonate in aqueous solution. That from the strychnine salt had $[\alpha]_D^{25°}$ + 5·2° ± 0·1° (Found : Na, 10·3%). That from the cinchonine salt had $[\alpha]_D^{25°}$ — 5·2° ± 0·2° (Found : Na, 10·4%).

α-Phenylbutyl bromide was obtained by passing hydrogen bromide through phenyl-*n*-propylcarbinol, prepared from benzaldehyde and magnesium *n*-propyl bromide (Grignard, *Ann. Chim. Phys.*, 1901, **24**, 466; Klages, *Ber.*, 1904, **37**, 2312). The bromide was thus obtained as a colourless, lachrymatory liquid, *d* about 1·24, b. p. 116°/28 mm., or 126°/47 mm. (Found : Br, 38·0. $C_{10}H_{13}Br$ requires Br, 37·6%).

Sodium α-Phenylbutanesulphonate.—The bromide (20 g.) was shaken with aqueous sodium sulphite at the ordinary temperature

for 135 hours. From the density of the residual oily layer, it was estimated that 60% of the bromide had been converted into α-phenyl-Δ^{α}-butene, 30% had remained unchanged, and 10% had reacted in the desired manner. Only 1·2 g. of sodium salt (yield about 6%) were obtained (Found : Na, 9·6. $C_{10}H_{13}O_3SNa$ requires Na, 9·7%).

Action of Sulphur Dioxide on Magnesium α-Phenylbutyl Bromide.—The Grignard reagent obtained from α-phenylbutyl bromide (5·5 g.) was cooled in ice and salt, and saturated with sulphur dioxide. A white solid separated, but dissolved before the calculated quantity of sulphur dioxide had been used. The resulting yellow solution, when decomposed in the usual manner, gave an ethereal solution which, on evaporation, gave white crystals. These, when recrystallised from alcohol, melted at 96°, and consisted of the *sulphide*, $(PhPr^{\alpha}CH)_2S$ (Found : S, 10·5. $C_{20}H_{26}S$ requires S, 10·7%).

Sodium α-Methylpropanesulphonate.—α-Bromobutane (115 g.) was heated gently under reflux for 100 hours with aqueous sodium sulphite; it had then all disappeared. The solution obtained was evaporated in stages, the crude sulphonate being obtained as the most soluble fraction. Recrystallisation from water gave 65 g. (50% yield) of the *sodium* salt (Found : Na, 14·5. $C_4H_9O_3SNa$ requires Na, 14·4%). The salt forms colourless plates which are very soluble in cold water.

α-Methylpropanesulphonic acid was prepared by repeated evaporation of the sodium salt with hydrochloric acid. It forms colourless, hygroscopic, hexagonal plates. Half an equivalent of strychnine was dissolved in an aqueous-alcoholic solution of the acid. A *strychnine* salt separated on cooling, and this, after being recrystallised thrice from aqueous alcohol, formed white needles sparingly soluble in water, more soluble in aqueous alcohol (Found, by titration against 0·1*N*-NaOH : strychnine, 70·0. $C_{21}H_{22}O_2N_2,C_3H_{10}O_3S$ requires strychnine, 70·7%). A solution of 0·485 g. of the salt in 50 c.c. of 50% aqueous alcohol had $\alpha_D^{20^\circ}$ — 0·57° in a 2-dcm. tube, whence $[\alpha]_D^{20^\circ}$ — 29·3°.

The corresponding sodium salt was only obtained in a very small quantity, and a qualitative examination showed it to be dextrorotatory. The *cinchonine* salt of the acid could not be obtained crystalline.

Sodium sec.-*butyl sulphate* was obtained from methylethylcarbinol *via* the calcium salt, and crystallised from alcohol (Found : Na, 13·0. $C_4H_9O_4SNa$ requires Na, 13·1%).

Part of the investigation of α-methylpropanesulphonic acid and its salts was carried out by Mr. J. F. Shillito, B.Sc., who was respons-

ible for its partial resolution. The authors desire to thank the Research Grant Committee of the Society for grants in aid of this investigation.

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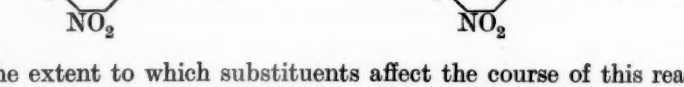
UNIVERSITY OF LONDON. [*Received, March 10th*, 1927.]

CLXII.—*The Scission of Diaryl Ethers and Related Compounds by means of Piperidine. Part I. The Scope of the Method and its Use in determining the Constitution of some Nitro-derivatives.*

By RAYMOND JAMES WOOD LE FÈVRE, SYDNEY LEONARD MORGAN SAUNDERS, and EUSTACE EBENEZER TURNER.

IT has been known for some time that ethers of nitrophenols react with ammonia, and with some of its mono- and di-substitution products, to give an alcohol (phenol) and a nitro-base :

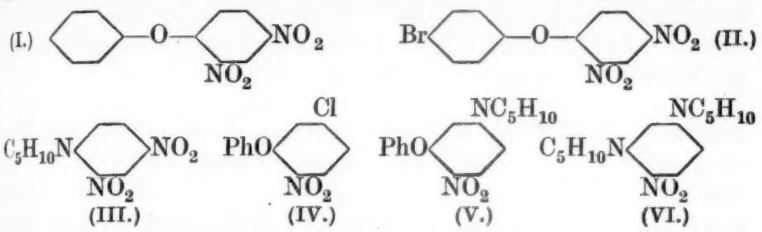


The extent to which substituents affect the course of this reaction is, however, a matter requiring investigation. Further, when R is a substituted aryl group, there is a possibility that a base such as piperidine may, in effecting the scission, which may now be written : $R{\cdot}O{\cdot}R' + C_5H_{10}NH \longrightarrow R{\cdot}NC_5H_{10} + R'{\cdot}OH$, give rise to more than two products. It should be possible, therefore, to use such reactions to compare the effects of different groups, or similar groups in different positions, on the strengths of attachment of the oxygen atom to the two benzene nuclei.

In order to determine the scope of the method, we have first investigated the behaviour towards piperidine of a number of substituted diphenyl ethers, some of which have been prepared for the purpose.

Diphenyl ether itself does not react with piperidine at 100°. 2- and 4-Nitrodiphenyl ether, and 2′-, 3′-, and 4′-chloro-2-nitrodiphenyl ether react slowly with piperidine at this temperature. On the other hand, 2 : 4-dinitrodiphenyl ether (I), 4′-bromo-2 : 4-dinitrodiphenyl ether (II), 2′ : 4′-dibromo-2 : 4-dinitrodiphenyl ether, and 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether give colorations in the cold with piperidine, which at 100° converts them in the course of a few minutes into mixtures of 2 : 4-dinitrophenylpiperidine

(Lellmann and Geller, *Ber.*, 1888, **21**, 2283) (III) and phenol, *p*-bromo-, 2 : 4-dibromo-, and 2 : 4-dinitro-phenol, respectively.



In 5-chloro-2-nitrodiphenyl ether (IV), the chlorine atom is more reactive than the phenoxyl radical, and by adjusting the conditions it is therefore possible to convert the ether first into *5-piperidino-2-nitrodiphenyl ether* (V) and then into 1-nitro-2 : 4-dipiperidinobenzene (VI).

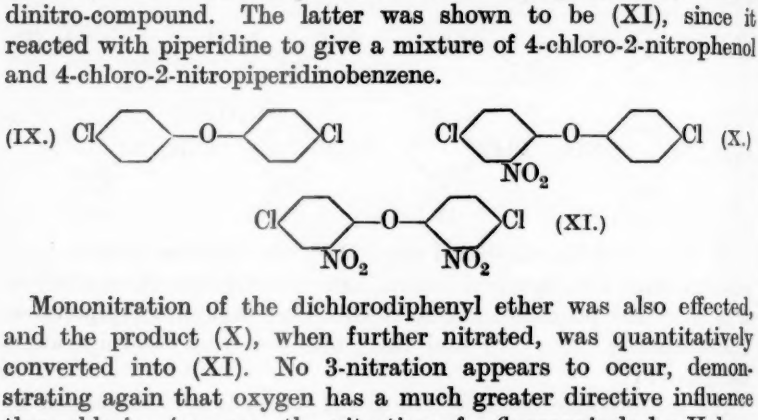
The considerable reactivity of diaryl ethers is well illustrated by the fact that we now find that 4-chloro-2 : 3′-dinitro-4′-phenoxydiphenyl (VII) and the corresponding 4-bromo-compound, both comparatively complex, are rapidly and quantitatively converted by piperidine at 100° into 4-chloro- (VIII) and 4-bromo-2 : 3′-dinitro-4′-piperidinodiphenyl respectively (compare Dennett and Turner, J., 1926, 476; Le Fèvre and Turner, *ibid.*, p. 1759).

Similarly, 3 : 3′-dinitro-4 : 4′-diphenoxydiphenyl is converted, though apparently more slowly, into 3 : 3′-dinitro-4 : 4′-dipiperidinodiphenyl.

2 : 4-Dinitrodiphenyl ether, when brominated, gave the 4′-bromo-derivative, the constitution of which follows (1) from its synthesis from 1-chloro-2 : 4-dinitrobenzene and potassium *p*-bromophenoxide, and (2) from its conversion, by piperidine, into *p*-bromophenol and 2 : 4-dinitrophenylpiperidine.

Hoffmeister (*Annalen*, 1871, **159**, 210), by the bromination of diphenyl ether, obtained a dibromo-derivative, m. p. 53—55°, which was regarded by Mailhe and Murat (*Bull. Soc. chim.*, 1912, **11**, 33), without supporting experimental evidence, as the 4 : 4′-compound. This constitution for the substance has now been established by synthesis. 4-Bromo-4′-nitrodiphenyl ether, obtained from potassium *p*-bromophenoxide and *p*-chloronitrobenzene, on reduction gave *4-bromo-4′-aminodiphenyl ether*, from which the 4 : 4′-dibromo-derivative was readily prepared. It melted at 60·5°, but repetition of Hoffmeister's experiments gave an identical substance.

4 : 4′-Dichlorodiphenyl ether (IX), synthesised in a similar manner, was converted by excess of cold fuming nitric acid into a dinitro-compound. The latter was shown to be (XI), since it reacted with piperidine to give a mixture of 4-chloro-2-nitrophenol and 4-chloro-2-nitropiperidinobenzene.



Mononitration of the dichlorodiphenyl ether was also effected, and the product (X), when further nitrated, was quantitatively converted into (XI). No 3-nitration appears to occur, demonstrating again that oxygen has a much greater directive influence than chlorine (compare the nitration of *o*-fluoroanisole by Holmes and Ingold, J., 1926, 1328). The present experiments incidentally establish the constitution of the product of direct chlorination of diphenyl ether (Mailhe and Murat, *loc. cit.*).

2-Nitrodiphenyl sulphide is unaffected by piperidine under conditions sufficing to effect partial scission of 2-nitrodiphenyl ether. Similarly, 2 : 4-dinitro- and 2 : 4 : 6-trinitro-*N*-ethyldiphenylamine do not react with piperidine. *p*-Nitrophenol is unaffected when boiled for some time with piperidine. It is hoped to investigate such cases in greater detail.

EXPERIMENTAL.

Action of Piperidine on 2- *and* 4-*Nitrodiphenyl Ether and* 2′-, 3′-, *and* 4′-*Chloro*-2-*nitrodiphenyl Ether.*—These ethers were heated for 30 minutes at 100° with an excess of piperidine. In each case, slight reaction occurred, as was evidenced by the odour of phenol, phenol, *o*-, *m*-, and *p*-chlorophenols, respectively, after acidification. Interaction was, however, insufficiently complete to allow of the isolation of any definite piperidino-derivative from the reddish, oily products.

4-*Bromo*-2 : 4′-*dinitrodiphenyl Ether.*—When 10 g. of 2 : 4-dinitrodiphenyl ether were heated with 12·3 g. of bromine in glacial acetic acid in presence of sodium acetate at 100°, 12·5 g. of the bromodinitro-compound, m. p. 134—136·5°, were obtained. One crystallisation from glacial acetic acid raised the m. p. to 136—137·5°. Raiford and Colbert (*J. Amer. Chem. Soc.*, 1926, 48, 2652) give m. p. 138·5°.

2 : 4-*Dibromo*-2′ : 4′-*dinitrodiphenyl ether* was prepared by heating

a mixture of 10 g. of 2 : 4-dibromophenol, 1·1 g. of potassium hydroxide, and 4 g. of 1-chloro-2 : 4-dinitrobenzene at 100° for 1·5 hours. After being extracted with alkali and with water, the product separated from glacial acetic acid in pale yellow crystals (9·5 g.), m. p. 131° (Found: Br, 38·3. $C_{12}H_6O_5N_2Br_2$ requires Br, 38·3%).

Action of Piperidine on 2 : 4-*Dinitro-* (I), 4′-*Bromo*-2 : 4-*dinitro-* (II), 2′ : 4′-*Dibromo*-2 : 4-*dinitro-*, *and* 2 : 4 : 2′ : 4′-*Tetranitro-diphenyl Ether.*—Each of these ethers gave a yellow to red coloration with cold piperidine, and on warming, a vigorous reaction set in. The resulting solution, on dilution with water, gave almost pure 2 : 4-dinitrophenylpiperidine (Lellmann and Geller, *loc. cit.*). This, after one crystallisation from alcohol, had m. p. 92°. The four aqueous filtrates, when acidified, etc., gave phenol, *p*-bromophenol, 2 : 4-dibromophenol, and 2 : 4-dinitrophenol, respectively.

Action of Piperidine on 5-*Chloro*-2-*nitrodiphenyl Ether.*—(1) *Two mols. of piperidine.* To a solution of 2·5 g. (1 mol.) of the ether in 10 c.c. of chloroform were added 2·2 c.c. of piperidine (2·25 mols.) dissolved in 5 c.c. of chloroform. The mixture was boiled for 2 minutes, the chloroform removed by evaporation, and the residual oil left in a vacuum for a week, then washed with light petroleum, and crystallised from alcohol–light petroleum. 5-*Piperidino*-2-*nitrodiphenyl ether* was thus obtained in yellow needles, m. p. 86—86·5° (Found: N, 9·5. $C_{17}H_{18}O_3N_2$ requires N, 9·4%). (2) *Excess of piperidine.* On addition of the chloronitro-ether (2 g.) to 5 c.c. of piperidine and gentle warming, a definite reaction occurred; the solution soon set to a magma of crystals. The whole was heated for ½ hour; a clear reddish-brown solution then resulted. Dilution gave an oil, which, after being washed, was extracted with benzene. The extract was dried over sodium sulphate and evaporated, and the solid residue crystallised from alcohol. The orange crystals obtained melted at 67° and were identical (mixed melting point) with the product of interaction of 2 : 4-dichloro-1-nitrobenzene with piperidine (Le Fèvre and Turner, this vol., 1113).

4-*Bromo*-4′-*nitrodiphenyl Ether.*—*p*-Bromophenol, *p*-chloronitrobenzene, and potassium hydroxide, the last dissolved in the minimal quantity of water, were allowed to condense in the usual manner. After extraction and distillation in a vacuum, the *bromonitro-ether* crystallised from alcohol in colourless prisms, m. p. 60°, b. p. 230°/15 mm. (Found: Br, 27·3. $C_{12}H_8O_3NBr$ requires Br, 27·2%).

4-*Bromo*-4′-*aminodiphenyl Ether and* 4 : 4′-*Dibromodiphenyl Ether.*—The preceding nitro-compound, when reduced with water, iron powder, and ferric chloride, gave an 84% yield of the crude amino-

compound, which was at once diazotised and converted into the diazo-perbromide. This, when decomposed in hot glacial acetic acid, gave dibromodiphenyl ether, which, after crystallisation from alcohol, melted at 60°. This compound did not depress the m. p. of the product (m. p. 60·5°; b. p. 210°/11 mm.) obtained by direct bromination of diphenyl ether by Hoffmeister's method (*loc. cit.*).

Dinitration of 4 : 4′-*Dibromodiphenyl Ether*.—A solution of the dibromo-compound in 10 parts of nitric acid (*d* 1·5) was heated at 100° for ½ hour and then poured into water. The precipitated solid separated from glacial acetic acid in small needles, m. p. 167° (Found : Br, 38·0. $C_{12}H_6O_5N_2Br_2$ requires Br, 38·3%).

Mononitration of 4 : 4′-*Dibromodiphenyl Ether*.—A solution of 20 g. of dibromodiphenyl ether in glacial acetic acid was treated with one of 8 g. of potassium nitrate in concentrated sulphuric acid. The solution was warmed at 100° for an hour, then cooled, and kept. The crystalline deposit separated from glacial acetic acid in small prisms, m. p. 90—91° (Found : Br, 42·5. $C_{12}H_7O_3NBr_2$ requires Br, 42·9%).

4-*Chloro*-4′-*nitrodiphenyl Ether*.—Condensation, by the usual process, of *p*-chloronitrobenzene, *p*-chlorophenol, and potassium hydroxide gave a product which, after alkali-washing and distillation in a vacuum, was crystallised from alcohol; it then had m. p. 75·5—76° and b. p. 215°/12 mm.

4-*Chloro*-4′-*aminodiphenyl Ether*.—Reduction of the preceding nitro-compound with iron, water, and ferric chloride gave an almost theoretical yield of crude amine. The latter crystallised from alcohol in colourless prisms, m. p. 100° (Found : Cl, 16·0. $C_{12}H_{10}ONCl$ requires Cl, 16·2%).

4 : 4′-*Dichlorodiphenyl Ether*.—The amino-compound was diazotised and submitted to the Sandmeyer reaction; after the usual procedure, the dichloro-compound separated from alcohol in colourless needles, m. p. 30°.

Nitration of 4 : 4′-*Dichlorodiphenyl Ether*.—The dichloro-compound was dissolved in 10 parts of nitric acid (*d* 1·5), and the solution warmed gently for 15 minutes. On cooling, crystals separated. These crystallised from glacial acetic acid in slender, white needles, m. p. 152° (Found : Cl, 21·4. $C_{12}H_6O_5N_2Cl_2$ requires Cl, 21·6%).

The dinitro-compound was dissolved in excess of piperidine, and the solution was boiled for 10 minutes. Dilution and filtration gave a solid, which, after being crystallised from glacial acetic acid, melted at 48° and was identical with 4-chloro-2-nitropiperidinobenzene (Le Fèvre and Turner, *loc. cit.*).

The filtrate from the above solid was acidified, and submitted to steam distillation; 4-chloro-2-nitrophenol then passed over. Its

identity was established by comparison with a sample prepared by heating 2 : 5-dichloronitrobenzene with 50% aqueous potassium hydroxide at the b. p. for 2 hours. Both specimens, and a mixture, melted at 87—88°.

Mononitration of 4 : 4′-*Dichlorodiphenyl Ether.*—To a solution of the dichloro-ether in glacial acetic acid was added a solution of 1·25 mols. of potassium nitrate in concentrated sulphuric acid. The mixture was warmed on the water-bath for an hour and diluted, and the precipitate was collected. It crystallised from alcohol in wads of short, white needles, m. p. 75°. Its m. p. was unaffected by admixture with a specimen prepared as follows : *p*-Chlorophenol, 2 : 5-dichloronitrobenzene, and potassium hydroxide were condensed together in the usual manner, and gave a product which, after extraction with alkali, boiled at 215—220°/15 mm. After crystallisation from alcohol, it had m. p. 75°.

Nitration of 4 : 4′-*Dichloro*-2-*nitrodiphenyl Ether.*—A solution of the nitro-compound in 10 parts of fuming nitric acid (*d* 1·5) was warmed for 10 minutes and then diluted. Filtration, followed by crystallisation from glacial acetic acid, gave the dinitro-compound, m. p. 152°, identical (mixed m. p.) with that obtained above from 4 : 4′-dichlorodiphenyl ether.

One of us (R. J. W. Le F.) has pleasure in acknowledging a maintenance grant from the Department of Scientific and Industrial Research, and the receipt of a grant from the Research Fund of the Chemical Society.

East London College,
University of London. [*Received, March 24th,* 1927.]

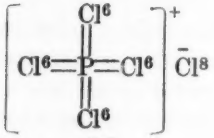
CLXIII.—*The Parachor and Chemical Constitution. Part V. Evidence for the Existence of Singlet Linkages in the Pentachlorides of Phosphorus and Antimony.*

By Samuel Sugden.

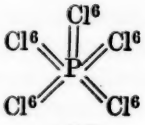
Some time ago Dr. N. V. Sidgwick suggested to the author that it would be of interest to examine the parachors of substances in which a central atom appears to share electrons with more than four other atoms. Substances of this type have a particular interest from the point of view of the electronic theory of valency, for it is difficult to formulate them satisfactorily without abandoning the octet rule or the conception of the sharing of electrons in pairs.

Three electronic formulæ have been suggested for phosphorus

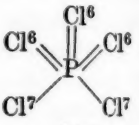
pentachloride. The polar formula (I) (Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 919) is open to many criticisms : phosphorus pentachloride is readily fusible (under pressure) and volatile, its solutions



(I.)



(II.)



(III.)

For this method of formulation the author is indebted to Dr. J. D. Main Smith. Each bond indicates a shared electron, whilst the superscript figures give the number of unshared electrons.

do not conduct electricity, and in general the substance has none of the properties of a salt. For these reasons, Lewis (" Valence and the Structure of Atoms and Molecules," 1923, p. 101) adopts formula (II) and considers that substances of this type are exceptions to the octet rule. On the other hand, Prideaux (*Chem. and Ind.*, 1923, **42**, 672) maintains the rule of eight by discarding the duplet rule for two of the chlorine atoms which are supposed to be bound by sharing one electron each with the phosphorus atom, as shown in formula (III).

This conception of a single-electron linkage (which for brevity will be termed a singlet), in which one electron is held in common by two atoms, played an important part in the earlier electronic theories of Stark ("Atomdynamik," Hirzel, Leipzig, 1916) and was suggested by Thomson (*Phil. Mag.*, 1921, **41**, 510) for the hypothetical NCl_5. More recently, Prideaux's formula for phosphorus pentachloride has been applied by Ingold and Ingold (J., 1926, 1315) to explain certain cases of substitution in the aromatic series. As these authors point out, the singlet linkage in this compound is a semipolar single bond, for it consists of half a covalency and half an electrovalency. If a shared electron is counted as half value for each of the atoms which share it (Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285), there is found to be a positive charge on the phosphorus atom and an effective half negative charge on each of the chlorine atoms held by a singlet. This half charge does not, of course, signify a splitting of the electron, but may be interpreted dynamically on the lines suggested by Højendahl (J., 1924, **125**, 1381) as a statistical average obtained by integrating the field of the electron in the neighbourhood of a particular atom over a time interval which is large compared with the period of revolution in its orbit. From this point of view it is obvious that the effective polarity of a shared electron will only be exactly 0·5 if its orbit lies

symmetrically about or between the two atoms which share it; the small variations in polarity discussed by Højendahl on this basis need not be considered here, and, with this reservation, the value 0·5 will be used in calculating polarities.

The most important difference between the point of view expressed by formulæ (II) and (III) is that in (II) the duplet is maintained and the octet rule abandoned, whilst in (III) the octet is completed by violating the rule that electrons are shared only in pairs. It is therefore of interest to inquire what general experimental evidence can be adduced in favour of these two hypotheses. The conception of duplets (Lewis, *loc. cit.*) is based upon (*a*) the occurrence of electrons in pairs at each quantum level throughout the structure of atoms, and (*b*) the presence of an even number of valency electrons in by far the greater number of stable molecules. This, however, can scarcely be regarded as proving the invariable covalency linkage of two electrons. Sufficient "odd" molecules exist to show that the pairing of electrons, although very common, is not necessary for the formation of stable molecules; also pairs of singlet linkages, as in formula (III), may well be present in molecules containing an even number of valency electrons.

On the other hand, the rule of eight can now be supported by a much greater body of experimental evidence. It is an essential feature of Bohr's theory of atomic structure that all the inert gases contain eight electrons of greatest principal quantum number. This conception is retained in the further sub-division into grouplets (Main Smith, "Chemistry and Atomic Structure," Benn, 1924; Stoner, *Phil. Mag.*, 1924, **48**, 719), which has now been shown to give a satisfactory explanation of *X*-ray absorption edges and the complex phenomena of multiplet structure in optical spectra. The volume of physical evidence in favour of the Bohr–Main Smith–Stoner scheme of the distribution of extra-nuclear electrons is now so large that it is highly improbable that any further advance in knowledge will necessitate a serious modification of its main features.

The octet rule has also been shown to predict accurately the occurrence and number of semipolar double bonds in a series of compounds of nitrogen, phosphorus, and sulphur (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525) and further striking evidence for the existence of this type of linkage has been obtained by the preparation of three new types of optically active sulphur compounds by Phillips and his collaborators (J., 1925, **127**, 2522; 1926, 2079; this vol., p. 188). In all these cases the existence of the semipolar double bond indicates that the number of electrons associated with the atoms of nitrogen, phosphorus, and sulphur does not exceed eight.

From these considerations, it appears probable that in compounds of the type of phosphorus pentachloride the rule of eight will still be valid and that (III) represents the structure of this compound better than (II). It is evident, however, that the case for the existence of singlet linkages would be very much strengthened if this rather indirect evidence could be supported by observation of an effect due directly to the presence of singlets. Such evidence is now furnished by the effect of singlets upon the parachor.

The Parachor and Singlet Linkages.

It has been shown (Sugden and Wilkins, this vol., p. 139) that the effect of unsaturated linkages upon the parachor is very nearly proportional to the excess of electrons above two in the linkage considered. Some of the values found are in Table I; the constants for ring structures are not recorded, but they lie between those found for the non-polar double and the single bond, and they can be predicted with fair accuracy on the assumption that they are proportional to the degree of unsaturation.

TABLE I.

Linkage.	No. of electrons.	Parachor.
Triple bond	6	46·6
Non-polar double bond	4	23·2
Single bond (duplet)	2	(0·0)
Semipolar double bond	2	−1·6
Singlet	1	−11·6
Semipolar single bond	1	−12·4

The duplet linkage (the chemical single bond) is of necessity neglected when the atomic constants are computed and must therefore be regarded as an arbitrary zero or normal level from which the effect of other linkages is measured. For the double and the triple bond and for ring structures, each electron above two adds 11·6 units to the molecular parachor; it seems probable, therefore, that this scale can be extended downwards and that the singlet linkage containing one electron less than the duplet will lower the parachor by 11·6 units. When a half-polar bond is present, as in phosphorus pentachloride, there must be added to this the effect of half a polar linkage, which, by comparison with the value for a semipolar double bond (duplet + polar bond), will be − 0·8. The total effect for a semipolar single bond should therefore be − 12·4 units. The singlet linkage is not always polar (compare the formula for acetylacetone derivatives, VIII, p. 1179) and when neutral would have a value of − 11·6 units; the difference is, however, less than the usual error of experiment. The two singlets in formula (III) should therefore give a change of − 24·8 in the molecular parachor.

The polar bond in formula (I) should produce an effect of — 1·6 units only. This value is obtained from the observed effect of the semipolar double bond which consists of a covalency plus an electrovalency. Since a covalency = 0, it follows that an electrovalency = — 1·6. Further evidence for this value is given by the parachors of the halogen hydrides recorded in Table II, calculated from the observations of Steele, McIntosh, and Archibald (*Z. physikal. Chem.*, 1906, **55**, 145). The surface-tension determinations of these workers are based upon the data of Ramsay and Shields and have therefore been corrected as indicated in an earlier paper (Sugden, J., 1924, **125**, 33). This correction increases the value of the parachor by about 1%.

TABLE II.

Substance.	[*P*]obs.	Σ[*P*].	Polar bond.
HCl	67·8	71·4	−3·6
HBr	85·4	85·1	+0·3
HI	105·3	108·1	−2·8
		Mean	−2·0

It is evident that these substances give the same structural constant as the semipolar double bond within the limits of experimental error (± 2 units). It is possible, of course, to argue that in the liquid state the halogen acids are not polarised and that the hydrogen atom is linked by a covalency. On this view, however, the structural constant for formula (I) would also be negligibly small, for it appears highly improbable that liquid phosphorus pentachloride is polar whilst liquid hydrogen chloride is not. A fuller discussion of this point will be given in a later paper in which the data for fused salts will be discussed.

The effect of the enhanced valency shell in formula (II) is rather more difficult to predict. The relation set out in Table I appears to be interpreted most simply by assuming that the effect of linkages upon the parachor is determined chiefly by the space required to accommodate the orbits of the shared electrons, and is very nearly a linear function of the number of shared electrons. On this view, the effect of the structure in (II) may be estimated roughly as follows. Since two extra electrons are shared between six atoms, the effect should be one-third of that found when two extra electrons are shared between two atoms in the non-polar double bond, *i.e.*, 23·2/3 or + 7·7 units.

The parachors for the pentachlorides of antimony and phosphorus have now been determined and are recorded in Table III. The column headed Σ[*P*] gives the sum of the atomic constants, and the last column shows the difference between [*P*]obs. and Σ[*P*], thus giving the effect of any special structure present in the mole-

TABLE III.

Substance.	$[P]$obs.	$\Sigma[P]$.	Structural constant.
Phosphorus pentachloride ...	282·5	309·2	−26·7
Antimony pentachloride	311·8	337·5	−25·7

cule. It will be seen that for both substances the value found for the structural constant is very close to the predicted effect of two singlet linkages, but differs widely from the expected effect of the structures represented by formulæ (I) and (II).

The atomic constant of phosphorus, used in calculating $\Sigma[P]$, has been determined from a number of compounds of this element for which data have already been recorded (Sugden, Reed, and Wilkins, *loc. cit.*). The constant for antimony was obtained from the data shown in Table IV in which $\Sigma[P]$ is the sum of all the atomic and structural constants in the molecule except that for the antimony atom. The mean value, 66·0, can scarcely be in error by more than $\pm$ 2 units.

TABLE IV.

Substance.	$[P]$obs.	$\Sigma[P]$.	Antimony.
Antimony trichloride	227·4	162·9	64·5
Triphenylstibine	637·4	570·0	67·4
		Mean	66·0

It should be mentioned that the anomaly exhibited in Table III cannot be accounted for by association of the liquid pentachlorides. Highly associated liquids, *e.g.*, alcohols, have a parachor which is only a few units below the predicted value and which increases as the temperature rises, but the pentachlorides examined show no signs of association—the parachor is nearly independent of temperature and the molecular weights of these substances in organic solvents are normal.

The difference between $[P]$obs. and $\Sigma[P]$ is therefore real, and since the additive nature of the parachor has been verified for a large number of substances, the conclusion seems inevitable that in these pentachlorides a type of valency linkage is present which has not been encountered in earlier work. It is submitted that by far the simplest interpretation of this result, which is in harmony with the established effect of well-known types of valency linkage, is the hypothesis that two singlet linkages are present in the molecule.

If this conclusion is accepted, it follows that the existence of singlet linkages can be detected, and their number determined, by means of the parachor. The extension of the electronic theory of valency to include singlet linkages, or more generally odd-electron linkages, can therefore be subjected to a direct experimental test and has no longer a purely speculative basis; it opens up a wide field for future investigation, as will be seen from the following brief account of the more important theoretical consequences.

Applications of the Theory of Odd-electron Linkages.

The formulæ suggested below are based upon the following three rules:

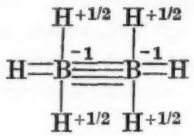
(1) The number of electrons associated with each atom (except hydrogen) does not exceed, and wherever possible is equal to, eight (the octet rule of Lewis).

(2) Atoms may share 1, 2, 3, 4, 5, or 6 electrons with another atom.

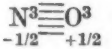
(3) The polarity of an atom in a compound is calculated by reckoning shared electrons at half their value, as proposed by Lowry (*loc. cit.*). When alternative formulæ are possible, the one showing the smallest development of polarity is the more probable.

Simple Compounds.—The application of the theory of odd-electron linkages to compounds of the type of SF_6, SCl_4, IF_5, ICl_3, OsF_8, etc., is obvious and has already been discussed by Prideaux (*loc. cit.*). Less obvious is the fact that borethane (IV) and nitric oxide (V) can be formulated with complete octets. Thomson's symmetrical formula for benzene (compare Sugden and Wilkins, J., 1925, **127**, 2518) also involves triplet linkages.

(IV.)

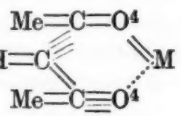


(V.)

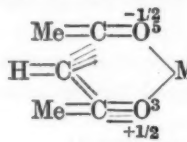


Chelate Linkages.—Singlet linkages give a simple explanation of the hypothetical residual valency bonds assumed to exist in many chelate groups. The oxalyl radical and ethylenediamine can, of course, be linked by two duplets, but in acetylacetone derivatives the metal is supposed to be attached to the second oxygen atom by a residual valency often indicated by a dotted line. This is shown in (VI) in which M represents one equivalent of a metal. The metal can, however, be attached to both oxygen atoms by singlets as in (VII); this formula contains polar oxygen atoms which can be neutralised by replacing the two double bonds by four triplets as in (VIII), in which all the atoms are neutral.

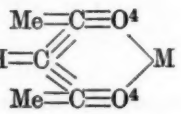
(VI.)



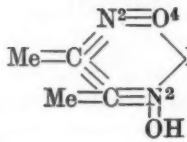
(VII.)



(VIII.)



(IX.)



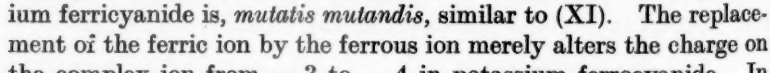
Formula (IX) represents in similar fashion the structure of derivatives of dimethylglyoxime, and gives a neutral molecule in which all the atoms, except hydrogen, have complete octets. It will be seen that the metal is co-ordinated with oxygen and nitrogen; if it is co-ordinated with the two oxygen atoms it incurs unlikely polarities.

Co-ordination Compounds.—In the older form of the electron theory of valency the existence of co-ordination numbers higher than 4 seemed to necessitate the abandonment of the octet rule. If singlet linkages are used, co-ordination numbers of 5, 6, 7, and 8 can readily be accounted for by the presence of 2, 4, 6, and 8 singlet linkages, respectively.

The cobaltammines and similar compounds can easily be formulated by building up an octet in the valency shell of the ion of the metal. This involves the assumption, first put forward by Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 762) and elaborated by Bury (*ibid.*, 1921, **43**, 1602), that the electronic structure of the transition elements is not uniquely determined. This suggestion has been verified by recent work on optical spectra, and the table of electronic configurations compiled by McLennan, McLay, and Smith (*Proc. Roy. Soc.*, 1926, **112**, 76) contains a number of examples of alternative structures which give rise to different groups of lines in the spectra of one element.

The structures of hexamminocobaltic chloride and potassium hexachlorocobaltiate are represented on this view by (X) and (XI). The polarities of the atoms are indicated in the formulæ, and it will be seen that in both cases the central cobalt atom has a net charge of -1, since its original charge of $+3$ is more than neutralised by sharing 8 electrons with the co-ordinated groups. The net charge of the complex ion as a whole is predicted correctly by summing the polarity of each group as indicated in the formulæ.

The corresponding derivatives of iron, chromium, and nickel can readily be formulated in a similar manner. The formula for potassium ferricyanide is, *mutatis mutandis*, similar to (XI). The replacement of the ferric ion by the ferrous ion merely alters the charge on the complex ion from -3 to -4 in potassium ferrocyanide. In all these formulæ a definite structure in harmony with the octet rule is assigned to the complex within Werner's square brackets



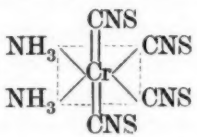
(X.) (XI.)

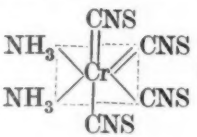
by substituting singlet linkages for the less clearly-defined "residual affinities." The recent work of Burgess and Lowry (J., 1924, **125**,

2081), Mills and Gotts (J., 1926, 3121), and Mann and Pope (*ibid.*, p. 2675) shows clearly that residual affinities are sufficiently well-defined entities to be capable of bringing about molecular asymmetry, and in all the compounds studied by these investigators singlet linkages can be employed to give a concrete picture of the bonds which are presumed to be responsible for the development of optical activity.

It would appear at first that formula (X) would give too many isomerides for co-ordination compounds containing two or more different radicals within the complex. The restrictions of the polarity rule (p. 1179), which means in this case that the duplet linkages are, wherever possible, associated with negative groups, reduce the number of possible isomerides in most cases to that which would be expected on the usual theory of a symmetrical octahedral structure. One interesting difference is found for substances of the type of Reinecke's salt, $NH_4[Cr(CNS)_4(NH_3)_2]$, which on the singlet theory might exist in two forms, (XII) and (XIII); the second of these, in which the duplets are *cis*, should be resolvable.

(XII.)



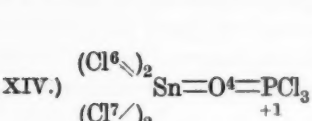


(XIII.)

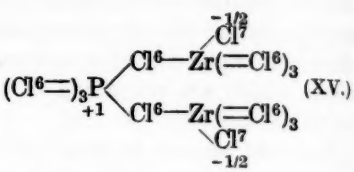
Since, however, a duplet linkage is much more bulky than a singlet, it appears probable that the normal form has the *trans*-structure (XII).

Molecular Compounds.—A large number of additive compounds, formed by the higher halides of Groups IV, V, and VI, are not readily formulated on Werner's co-ordination theory; some of these possess an extraordinary stability, *e.g.*, $SnCl_4,POCl_3$, b. p. 180°; $2ZrCl_4,PCl_5$, b. p. 416°; $2ZrCl_4,POCl_3$, b. p. 363°. All these compounds can be formulated by using singlet linkages. In general, the formulæ are obtained by supposing that two of the halogen atoms in one molecule, which were originally linked by duplets, become linked by singlets; the central atom is then sharing only 6 electrons and can link with a lone pair of electrons in the second compound. Formula (XIV) gives such a structure for $SnCl_4,POCl_3$; similar formulæ account for the well-known series of additive compounds of stannic chloride with ketones which have the composition $SnCl_4,2R_1R_2CO$. In the corresponding series of compounds with antimony pentachloride, the compounds so far described have the compositions $SbCl_5,R_1R_2CO$ or $2SbCl_5,3R_1R_2CO$; these are exactly the compounds to be expected if the linkage between the molecules is made possible by the conversion of halogens linked by duplets

into halogens linked by singlets. The very stable compound $2ZrCl_4,PCl_5$ appears to be of a rather different type in which each



(XIV.)



(XV.)

of the chlorine atoms originally linked by singlets shares an electron with a zirconium atom (XV). A similar structure can be written for the corresponding compound with phosphorus oxychloride.

Finally, the singlet linkage gives a concrete picture of the vague term " residual affinity " used to explain so many chemical changes, *e.g.*, the Wagner–Meerwein transformation, the *trans* Beckmann change, etc.; in many of the theories of these reactions, in which a residual affinity becomes a complete covalency after a series of changes, the use of singlet linkages gives a clearer picture of the mechanism of the reaction. Another interesting aspect of the singlet, when it forms a semipolar single bond, is that it is a definite half-way stage between a covalency and a polar valency.

Sufficient has been said to show that the theory of odd-electron linkages here put forward is capable of simplifying and correlating a large body of chemical knowledge. Furthermore, it leads to conclusions (*e.g.*, the magnitude of the parachor) which can be subjected to an experimental test, and therefore fulfils all the requirements of a sound working hypothesis. In succeeding papers of this series it is hoped to apply this and other tests to a number of the substances formulated above; many of them are fusible without decomposition and can therefore be dealt with by the experimental methods described in this and other papers on the parachor.

Experimental.

In the course of this investigation measurements have been made of the surface tension and density of phosphorus pentachloride, antimony trichloride, and antimony pentachloride. From these, the parachors were calculated by the relation $P = \gamma^{1/4}/(D - d)$, where γ is the surface tension, and D and d are the densities of the liquid and saturated vapour, respectively.

Phosphorus pentachloride was purified by sublimation and stored in sealed tubes. It melted in a closed tube at 163—164° (corr.), which is much higher than the value, *viz.*, 148°, given by Casselmann (*Annalen*, 1852, **83**, 247). A small infusible residue remained when a quantity of the substance was melted; this appeared to be

insoluble in the liquid and since its amount was small it is believed not to have any serious effect upon the surface-tension or density measurements.

Since the pentachloride has a large vapour pressure at its melting point, all the measurements had to be carried out in sealed vessels. The density of the liquid was therefore determined by the method of flotation. Small glass floats about $5 \times 1 \times 1$ mm. were prepared and the temperature was determined (to the nearest 0·5°) at which they were in equilibrium with a suitable mixture of bromoform and benzene. The density of the liquid at this temperature was then determined by means of a pyknometer.

Each float was placed in a marked piece of quill tubing sealed at one end. One of the storage tubes was then broken and the open end of the quill tube forced into the mass of pentachloride until a sufficient quantity of the substance had been picked up; the pentachloride was rapidly tapped down to the closed end, and the tube sealed off. In this way exposure to the atmosphere for more than a few seconds was avoided and only a negligible quantity of moisture could have been absorbed.

Tubes filled in this manner were supported in a glycerol-bath provided with a thermometer and stirrer, and the temperatures of flotation were determined. Molten phosphorus pentachloride proved to be a mobile liquid and no difficulty was experienced in fixing the flotation temperatures to within $\pm$ 0·5°. The following results were obtained.

Float	1	5	6
Density	1·482	1·520	1·559
Flotation temp. (corr.)	218°	200·5°	181°

whence $D^{\cdot}_{\cdot} = 1{\cdot}624 - 0{\cdot}00208\,(t - 150)$.

A rough determination of the vapour pressure (dissociation pressure) was next made to ascertain the order of magnitude of the pressure within the tubes. This proved to be unexpectedly small, so that the density of the vapour could be calculated with sufficient accuracy from the vapour-pressure observations.

A quantity of the pentachloride was confined in a bulb of about 5 c.c. capacity connected to a capillary tube bent at right angles to give a long capillary limb. An index of mercury separated the gas in the bulb from a fixed quantity of air in the long limb of the apparatus; the distant end of the capillary tube was sealed whilst the whole apparatus was at a known temperature and at atmospheric pressure. The bulb was then heated in a glycerol-bath, and the volume of the air in the long limb measured by means of a millimetre scale. From this volume, the total pressure in the apparatus was calculated; by subtracting the pressure of the air

present initially in the bulb, the vapour pressure (in atm.) of the pentachloride was obtained.

t (corr.).	Reading.	p_{total}.	p_{air}.	p_{PCl_5}.
13°	24·3	1·00	1·00	—
142·5	14·1	1·72	1·45	0·27
163	11·1	2·41	1·52	0·67
182	8·1	3·00	1·59	1·41
195·5	6·6	3·68	1·64	2·03

These figures can only be regarded as a rough approximation, but they indicate that below 200° no great pressure is developed. From the results, the density of the vapour at the three temperatures used for the measurement of the surface tension was calculated as follows. If the gas laws can be assumed to hold for the vapour, the density is given by $d = Mp/RT$, where M is the molecular weight and p the pressure. For phosphorus pentachloride a correction must be applied for the degree of dissociation, α, so that the formula becomes, putting $M = 208{\cdot}3$ and expressing R in c.c.-atm., $d = 2{\cdot}54\ p/(1 - \alpha)T$. The pressure p was interpolated from the figures given above, whilst the dissociation constant K was obtained from the observations of Cahours (*Annalen*, 1867, **141**, 42). Incidentally, it may be noted that, since the degree of dissociation in the vapour is less than 50%, the dissociation of the liquid must be very small. The calculation of d is set out below; as the values found are small compared with the liquid density, they need not be known with great accuracy, since it is the quantity $(D - d)$ which is used in calculating the parachor.

t (corr.).	p (atm.).	K.	α.	d.	D.	$D - d$.
169·5°	0·78	0·175	0·43	0·0031	1·583	1·580
181	1·02	0·205	0·41	0·0041	1·560	1·556
192	1·81	0·255	0·35	0·0073	1·537	1·530

The surface tension was measured by the method of capillary rise, the apparatus and microscope fittings already described by the author (J., 1921, **119**, 1483) being used. Apparatus 3 was employed for which $r_1 = 0{\cdot}005495$ cm. and $r_2 = 0{\cdot}1310$ cm. The method of calculating a^2 from the capillary rise, H, was described in the above paper. The following results were obtained :

t (corr.).	H (mm.).	a^2 (mm.^{2}).	$D-d$ (g./c.c.).	γ (dynes/cm.).	Parachor.
169·5°	3·027	2·690	1·580	20·9	281·8
181	2·918	2·592	1·556	19·8	282·5
192	2·815	2·496	1·530	18·7	283·1
				Mean	282·5

[With ADOLPH FREIMAN.]

The surface tensions of antimony tri- and penta-chlorides were determined by the method of maximum bubble pressure (Sugden,

J., 1922, **121**, 858; 1924, **125**, 27). The tables are set out in the manner described in earlier papers of this series. The bubbler used was No. 16a, and had the following constants: $r_2 = 0{\cdot}179$ cm., $A = 0{\cdot}008271$.

Antimony trichloride, $M = 228{\cdot}2$, was purified by distillation and had b. p. 219° (corr.). Densities determined: $D_4^{95{\cdot}5°}$ 2·632, $D_4^{123{\cdot}5°}$ 2·565, $D_4^{149{\cdot}5°}$ 2·510; whence $D_4^{t°} = 2{\cdot}844 - 0{\cdot}00224t$. These densities are in good agreement with those found by Jaeger (*Z. anorg. Chem.*, **1917**, **101**, 1).

App.	t.	P.	D.	ϕ.	γ.	Parachor.
16a	109·5°	5067	2·599	1·0621	44·51	226·7
,,	127·5	4748	2·558	1·0653	41·84	226·9
,,	148·5	4462	2·511	1·0682	39·43	227·6
,,	166·5	4219	2·471	1·0710	37·38	228·3
					Mean	227·4

Antimony pentachloride, $M = 298{\cdot}1$, was distilled under diminished pressure; the fraction used boiled at 85° (corr.)/55 mm. Owing to the hygroscopic nature of this substance the densities were measured by using a sealed dilatometer. Densities determined: $D_4^{11{\cdot}5°}$ 2·370, $D_4^{16°}$ 2·358, $D_4^{36°}$ 2·319, $D_4^{52°}$ 2·289, $D_4^{78°}$ 2·231; whence $D_4^{t°} = 2{\cdot}392 - 0{\cdot}00204t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
16a	15·5	4130	2·360	1·0692	36·53	311·5
,,	36	3938	2·318	1·0713	34·90	312·5
,,	56	3605	2·278	1·0765	32·11	311·4
,,	68	3447	2·253	1·0792	30·78	311·6
					Mean	311·8

Triphenylstibine, $M = 353{\cdot}0$. The following data are taken from the work of Walden and Swinne (*Z. physikal. Chem.*, 1912, **79**, 700). Since these investigators used Ramsay and Shields's value for benzene in standardising their apparatus, the surface tensions are corrected by multiplying by 1·0335 (Sugden, J., 1924, **125**, 34).

t.	γ.	γ (corr.).	D.	Parachor.
35·1	41·63	43·01	1·4200	636·6
47·0	40·58	41·93	1·4105	637·0
63·1	39·08	40·38	1·3952	637·7
77·3	37·60	38·85	1·3820	637·9
91·2	36·12	37·32	1·3683	637·7
103·0	34·92	36·08	1·3568	637·7
				Mean 637·4

Summary.

(1) The parachors of phosphorus and antimony pentachlorides have been determined and are 26 units below the sum of the atomic constants.

(2) Three formulæ for the structure of these substances from the standpoint of electronic valency theory have been discussed, and

the effect of each upon the parachor has been deduced by the aid of the relation between the parachor and the number of electrons in a linkage.

(3) The formula of Prideaux, in which two singlet linkages are present, is considered to give the best and simplest explanation of the observed anomaly. The parachor can therefore be used to detect the presence of such linkages, since each singlet linkage contributes — 12·4 units to this molecular constant.

(4) The electronic theory has been extended to include linkages composed of odd numbers of shared electrons. The modified theory has been applied to deduce formulæ for the higher halides of Groups V, VI, VII, and VIII, for borethane, nitric oxide, chelate groups, co-ordination compounds, and for a number of "molecular compounds."

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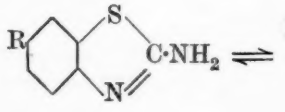
CLXIV.—*Aminobenzthiazoles. Part VIII. The Effect of Polar Substituents on the Formation and Stability of Nuclear-substituted* 1-*Aminobenzthiazole Bromides.*

By GEORGE MALCOLM DYSON, ROBERT FERGUS HUNTER, and RICHARD WILLIAM MORRIS.

IT appeared probable that valuable evidence for the view that the bromine atoms in the benzthiazole dibromides are held to the nuclear nitrogen atom by means of single electrons (compare Ingold and Ingold, J., 1926, 1385) might be obtained by a study of the effect of different polar substituents on the formation and stability of these compounds. The examination of the bromides of the 5-substituted 1-aminobenzthiazoles (I ⇌ II) was therefore undertaken.

(I.)  (II.)

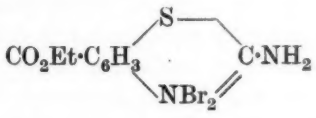
In accordance with the suggested electronic constitutions of these bromo-addition compounds, it was found that negative groups, such

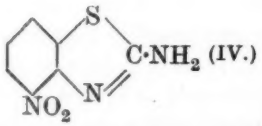
as the cyano- and the carbethoxy-group (R = CN, CO_2Et, etc.), tended to stabilise the NBr_2 complex in the bromides, whilst positive groups, such as the ethoxy- and the methoxy-group (R = OEt, OMe, etc.), had the reverse effect. The stability of the bromides could not be investigated quantitatively, but atmospheric decomposition of the compounds indicated that the effects of the substituents conform to "general polarity," the series being CN,CO_2Et> Br,Cl> OEt,OMe in order of decreasing stability of the bromide. This series is similar to that recorded by Rule and Paterson (J., 1924, **125**, 2155), and by Rule and Smith (J., 1925, **127**, 2188) denoting the relative influence of groups on acidic strengths of aliphatic acids and on velocity of reaction and molecular inductive capacity.

The 5-substituted 1-aminobenzthiazole bromides were obtained by bromination of the corresponding *p*-substituted phenylthiocarbamides in chloroform (Hunter, J., 1925, **127**, 2023, and later papers). These reacted much more slowly than phenylthiocarbamide and its homologues (J., 1926, 1385), resembling in this respect the *s*-*p*-bromophenylalkylthiocarbamides (Hunter and Soyka, J., 1926, 2958), owing possibly to the greater stability of the intermediate ·CBr·SBr compound (Hugershoff, *Ber.*, 1903, **36**, 3121; Hunter and Soyka, *loc. cit.*).

Under the usual conditions of bromination, *p*-cyanophenylthiocarbamide yielded a *tetrabromide* of 1-amino-5-cyanobenzthiazole, which on reduction gave the 5-cyano-base (I ⇌ II; R = CN). 1-*Amino-5-cyanobenzthiazole*, however, on bromination in chloroform, gave a well-defined *hexabromide*, from which four labile bromine atoms were readily removed by ammonia (compare Macbeth and Hirst, J., 1922, **121**, 904; Macbeth, *ibid.*, p. 1116, and later papers).

Bromination of *p*-carbethoxyphenylthiocarbamide produced a *dibromide* (III) of 1-amino-5-carbethoxybenzthiazole, whereas bromination of 1-amino-5-carbethoxybenzthiazole itself (I ⇌ II; R = CO_2Et) gave a *tribromide*, which is doubtless analogous to the tribromides of the 3-thiol-5-keto-2 : 4-dialkyltetrahydro-1 : 2 : 4-thiodiazoles (Freund and Asbrand, *Annalen*, 1895, **285**, 166; Freund and Bachrach, *ibid.*, p. 184).

(III.) 

 (IV.)

p-Chlorophenylthiocarbamide resembled *p*-carbethoxyphenylthiocarbamide in giving a *dibromide* (of 5-chloro-1-aminobenzthiazole; formula as III), but bromination in chloroform of 5-chloro-1-amino-

benzthiazole gave rise to a *hexabromide* similar to that obtained from 1-amino-5-cyanobenzthiazole. Acetylation of the amino-group in 5-chloro-1-aminobenzthiazole, however, somewhat decreased the reactivity of the heterocyclic nucleus, for 5-*chloro*-1-*acetamido-benzthiazole* yielded a *tetrabromide* on bromination under the usual conditions. Bromination of *p*-bromophenylthiocarbamide had previously been observed to give rise to a dibromide of 5-bromo-1-amino-benzthiazole (J., 1926, 1397); by using a higher concentration of bromine, a *tetrabromide*, analogous to the tetrabromide of 1-amino-5-cyanobenzthiazole, has now been isolated.

p-Ethoxyphenylthiocarbamide yielded, on bromination, a *pentabromide* of 1-amino-5-ethoxybenzthiazole, which is probably the hydrobromide of the tetrabromo-addition compound; whereas *p*-methoxyphenylthiocarbamide, under similar conditions, gave rise to a *dibromide* of 1-amino-5-methoxybenzthiazole (formula as III).

1-Amino-5-methylbenzthiazole (I $\rightleftharpoons$ II; R = Me), on bromination, gave an unstable *tetrabromide*, which lost bromine on exposure to air, giving a more stable *tribromide*.

Several unsuccessful attempts were made to prepare 5-dimethylamino-1-aminobenzthiazole (I $\rightleftharpoons$ II; R = NMe_2) by bromination of *p*-dimethylaminophenylthiocarbamide. The formation of a thiazole ring on a benzene nucleus is clearly a case of ortho-substitution and therefore must depend on the *o* : *p*-directive influence of the nitrogen atom which becomes the nuclear nitrogen atom of the dicyclic system. The dimethylamino-group in *p*-dimethylamino-phenylthiocarbamide is considerably more basic than the amino-group, and the tendency is, therefore, towards *o* : *p*-substitution with respect to the dimethylamino-group, that is, towards heterocyclic ring formation in the meta-position to the thiocarbamide complex. Such formation is doubtless impossible (compare Perkin and Titley, J., 1922, **121**, 1562; Titley, J., 1926, 508), and benzthiazole ring formation in this case is therefore inhibited.

p-Acetylphenylthiocarbamide behaved anomalously on bromination, yielding a bromo-addition compound which, on reduction with sulphurous acid, gave a complex substance free from sulphur, the exact nature of which has not yet been ascertained.

In view of the low reactivity of 5-nitro-1-phenylbenzthiazole towards bromine (Hunter, J., 1926, 538), the effect of the nitro-group on the unsaturation of the heterocyclic nucleus in 3-*nitro*-1-*amino-benzthiazole* (IV) was also examined. Under the usual conditions of bromination, *o*-nitrophenylthiocarbamide yielded what appeared to be a mixture of a tetrabromide and a tribromide of 3-nitro-1-aminobenzthiazole; on reduction in the usual way, this mixture yielded the base (IV). All attempts to brominate this nitroamino-

benzthiazole led only to uncrystallisable bromides, which were not investigated.

Experimental.

The arylthiocarbimides required for this work were obtained by adding a solution of the corresponding nuclear-substituted aniline (1 mol.) in chloroform to a well-stirred suspension of thiocarbonyl chloride (1·3 mols.) in water, and isolating the product in the usual way (Dyson and Hunter, *J. Soc. Chem. Ind.*, 1926, **45**, 83T). The arylthiocarbimides were converted into the corresponding thiocarbamides by treatment with alcoholic ammonia (*loc. cit.*) and were usually recrystallised from alcohol.

Bromination.—The thiocarbamide or the benzthiazole was dissolved in chloroform and treated slowly with a solution of bromine in the same solvent. The benzthiazole bromide separated, in some cases at once, in others after the mixture had been heated under reflux, hydrogen bromide being evolved.

1-*Amino*-5-*cyanobenzthiazole tetrabromide* (prepared from *p*-cyanophenylthiocarbamide, 1 g.; chloroform, 15 c.c.; bromine, 1 c.c.; time of refluxing, 10—15 minutes) separated as a reddish-brown, crystalline mass, which was collected on porous earthenware and dried in a vacuum over potassium hydroxide. On heating, it became yellow at 60—70°, colourless at about 150°, and melted to a black, viscous liquid at 236° (Found: Br, 64·0. $C_8H_5N_3Br_4S$ requires Br, 64·6%). The compound lost bromine slowly on exposure to moist air, becoming colourless after some days. It liberated iodine from dilute hydriodic acid (Hunter and Soyka, J., 1926, 2962).

1-*Amino*-5-*cyanobenzthiazole.*—The tetrabromide was suspended in sulphurous acid and treated with sulphur dioxide, and the colourless solution was filtered and treated with ammonia (*d* 0·880); the *base* then separated in white flakes. It crystallised from 50% alcohol in tufts of silky needles, m. p. 196° (Found: S, 18·3. $C_8H_5N_3S$ requires S, 18·3%). This compound was hydrolysed only with difficulty by acids and was usually recovered unchanged after treatment with hydrochloric acid under the usual conditions, this behaviour recalling the similiar properties of 5-cyano-1-phenylbenzthiazole (Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, **44**, 826).

1-*Amino*-5-*cyanobenzthiazole hexabromide* (prepared from the aminocyanobenzthiazole, 0·3 g.; chloroform, 10 c.c.; bromine, 0·3 c.c.; time of refluxing, 1 minute) separated in golden-brown plates, which, after being dried in a vacuum, gradually lightened in colour on heating and charred at about 290° (Found: Br, 74·0. $C_8H_5N_3Br_6S$ requires Br, 73·2%). This compound had the usual properties and was relatively stable to air. On treatment with

ammonia (*d* 0·880) it lost 2 mols. of bromine [Found : Br (labile), 48·4. $C_8H_5N_3Br_2S(Br_4)$ requires Br (labile), 48·9%].

1-*Amino*-5-*carbethoxybenzthiazole dibromide* (prepared from *p*-carbethoxyphenylthiocarbamide, 1 g.; chloroform, 20 c.c.; bromine, 1 c.c.; mixture refluxed) separated in small, red crystals which melted at 125° (decomp.) after being dried in a vacuum (Found: Br, 42·0. $C_{10}H_{10}O_2N_2Br_2S$ requires Br, 41·8%). The compound had the usual properties, but was relatively stable to air.

On one occasion, the bromination of *p*-carbethoxyphenylthiocarbamide gave rise to a red *tribromide*, m. p. 152° (decomp.) [Found : Br, 53·0. $(C_{10}H_{10}O_2N_2Br_3S)_2$ requires Br, 52·0%].

1-*Amino*-5-*carbethoxybenzthiazole*.—Either of the preceding bromides was suspended in sulphurous acid and treated with sulphur dioxide until the product was colourless when crushed. The product was then treated with ammonia (*d* 0·880), washed, dried, crystallised from alcohol, and recrystallised from alcohol–ethyl acetate (1 : 1); small, soft, glistening prisms, m. p. 242° (Found: S, 14·0. $C_{10}H_{10}O_2N_2S$ requires S, 14·4%), were thus obtained. On hydrolysis with hydrochloric acid, and extraction with ether, small crystals of 1-*amino*-5-*carboxybenzthiazole* were obtained, which did not melt on heating.

1-*Amino*-5-*carbethoxybenzthiazole tribromide* (prepared from the aminocarbethoxybenzthiazole, 0·2 g.; chloroform; bromine, 0·2 c.c.) separated as a red, crystalline mass. The dried substance turned yellow at 150—160°, became colourless on further heating, and melted at 247° (decomp.) [Found : Br, 51·7. $(C_{10}H_{10}O_2N_2Br_3S)_2$ requires Br, 51·9%]. This compound was relatively stable to air, and the labile bromine removed by ammonia (*d* 0·880) corresponded to 24%.

5-*Chloro*-1-*aminobenzthiazole dibromide* was prepared from *p*-chlorophenylthiocarbamide (1·5 g.) as a red, crystalline mass. After being dried, it became colourless at 135° and charred at 215° (Found : Br, 46·0. $C_7H_5N_2ClBr_2S$ requires Br, 46·5%). It had the usual properties and gradually lost bromine on exposure to air, becoming orange, yellow, and finally colourless.

5-*Chloro*-1-*aminobenzthiazole* was precipitated from the solution obtained from the reduction of the dibromide with sulphurous acid, by ammonia, in lustrous plates, m. p. 198°. On recrystallisation from 60% alcohol, it formed aggregates of small, glistening needles, m. p. 199° (Found : Cl, 19·0. $C_7H_5N_2ClS$ requires Cl, 19·2%). The *acetyl* derivative was obtained by boiling a solution of the base in acetic anhydride for a few minutes and pouring it into alcohol. It crystallised from alcohol–ethyl acetate (2 : 1) in small prisms, m. p. 225° (Found : Cl, 13·8. $C_9H_7ON_2ClS$ requires Cl, 15·7%).

5-*Chloro*-1-*aminobenzthiazole hexabromide* was obtained, by bromination of the base in chloroform with excess of bromine, in glistening, golden plates, which were unmelted at 270° (Found: Br, 73·0. $C_7H_5N_2ClBr_6S$ requires Br, 72·3%).

5-*Chloro*-1-*acetamidobenzthiazole tetrabromide* was obtained from 5-chloro-1-acetamidobenzthiazole in orange-yellow crystals, m. p. 215° (after drying) (Found: Br, 57·5. $C_9H_7ON_2ClBr_4S$ requires Br, 58·5%). It was relatively stable to moist air.

5-*Bromo*-1-*aminobenzthiazole tetrabromide*, prepared from *p*-bromophenylthiocarbamide by the method used in the case of 1-amino-5-cyanobenzthiazole tetrabromide, melted at 82—83° with effervescence, giving a yellow solid which became colourless at 170° and melted at 260—262° (decomp.; softening at 258°) (Found: Br, 73·0. $C_7H_5N_2Br_5S$ requires Br, 72·9%). On reduction with sulphurous acid, the tetrabromide yielded 5-bromo-1-aminobenzthiazole, m. p. 211° (Hunter, J., 1926, 1397).

1-*Amino*-5-*ethoxybenzthiazole tetrabromide hydrobromide*, prepared from 1 g. of *p*-ethoxyphenylthiocarbamide, separated in orange-coloured crystals. After being dried in a vacuum, it became colourless at 120—125° and charred at 200° (Found: Br, 67·8. $C_9H_{10}ON_2Br_4S,HBr$ requires Br, 67·3%).

1-*Amino*-5-*ethoxybenzthiazole*.—The preceding hydrobromide was dissolved in a large volume of sulphurous acid (saturated with sulphur dioxide at 15°), and the *base* precipitated with ammonia. After recrystallisation from alcohol–benzene (1 : 2) and from 50% alcohol, it was obtained in small, lustrous prisms, m. p. 174° (Found: S, 16·0. $C_9H_{10}ON_2S$ requires S, 16·5%).

1-*Amino*-5-*methoxybenzthiazole dibromide* (prepared from *p*-methoxyphenylthiocarbamide, 1 g.; chloroform, 20 c.c.; bromine, 1 c.c.) separated in dark brown granules. After drying in a vacuum, it became orange at 70—80°, colourless at 170°, and charred at 240° (Found: Br, 47·9. $C_8H_8ON_2Br_2S$ requires Br, 47·0%). It had the usual properties, but was very unstable and rapidly lost bromine on exposure to the atmosphere.

1-*Amino*-5-*methoxybenzthiazole* was obtained as in the case of the ethoxy-base, and crystallised from 50% alcohol in small, soft plates, m. p. 147° (Found: S, 17·5. $C_8H_8ON_2S$ requires S, 17·7%).

Bromination. The base (0·2 g.) was brominated in chloroform. A black, tarry mass was obtained which, on exposure to air for some days, yielded a violet solid. On heating, this substance became yellow, white and purple in turn and then melted at 220—225° (decomp.) (Found: Br, 48·1%).

1-*Amino*-5-*methylbenzthiazole Tetrabromide*.—One g. of 1-amino-5-methylbenzthiazole (m. p. 140°; Hunter, J., 1926, 1399) was

dissolved in 10 c.c. of chloroform and treated with bromine (1 c.c.), a reddish-brown tar (which rapidly solidified) being precipitated. The filtered solution deposited the *tetrabromide* in chocolate-brown plates with a golden lustre. After drying in a vacuum, the tetrabromide lightened in colour at about 180—190°, but was unmelted at 275° (Found : Br, 66·1. $C_8H_8N_2Br_4S$ requires Br, 66·1%). The compound had the usual properties and liberated iodine from a solution of potassium iodide in pure acetic acid. On exposure to air, it lost bromine, leaving a brown, granular, microcrystalline *tribromide*, m. p. 295° (decomp.) [Found : Br, 58·0. $(C_8H_8N_2Br_3S)_2$ requires Br, 59·4%]. This substance was relatively stable to air.

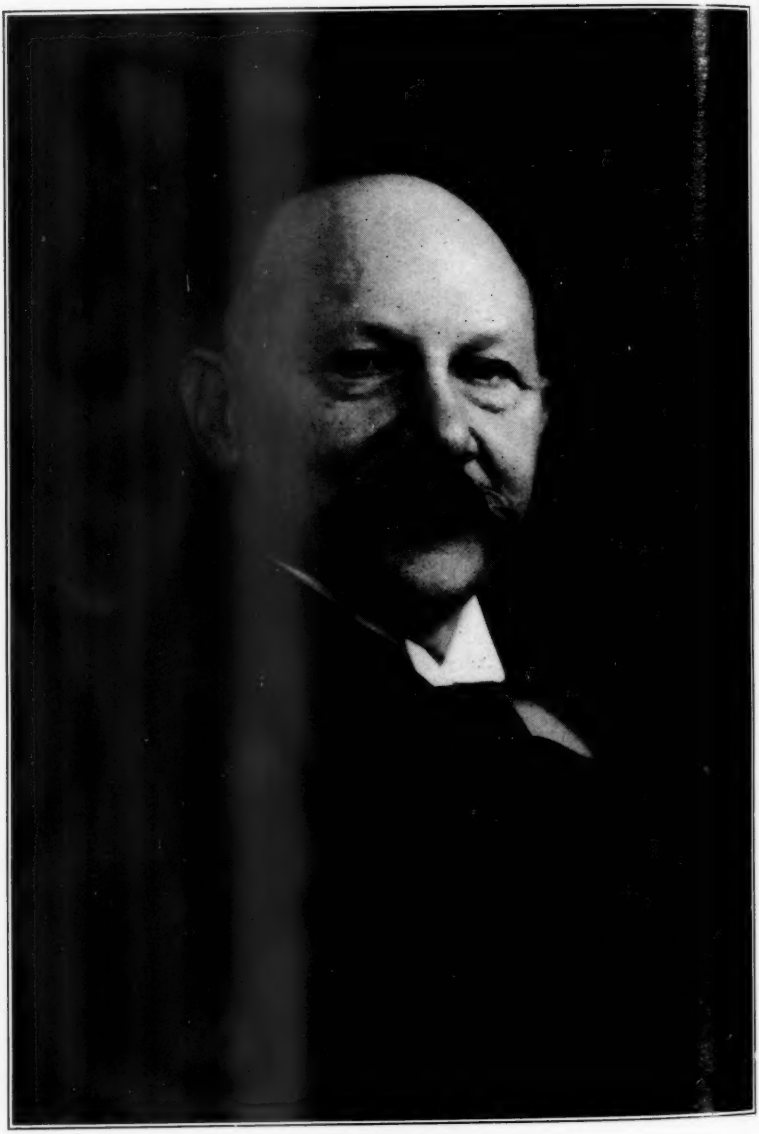
Bromination of p-*Acetylphenylthiocarbamide.*—One g. of *p*-acetylphenylthiocarbamide in chloroform (20 c.c.) was brominated in the usual way; hydrogen bromide was evolved and a bromo-addition compound separated as a bright yellow, crystalline solid, m. p. 137—140° (decomp.). On reduction with sulphurous acid, this yielded a pale yellow, insoluble solid which did not melt below 300°. This substance was free from sulphur, but contained bromine (Found : Br, 20·6%).

3-*Nitro*-1-*aminobenzthiazole.*—One g. of *o*-nitrophenylthiocarbamide was brominated in the usual way, and the mixture refluxed; hydrogen bromide was slowly evolved. The bromo-addition compound formed glistening, orange-brown crystals, m. p. 288° (decomp.), whose composition corresponded most closely with that of a tribromide [Found : Br, 57·2. $(C_7H_5O_2N_3Br_3S)_2$ requires Br, 55·1. $C_7H_5O_2N_3Br_4S$ requires Br, 62·1%]. On reduction with sulphurous acid, the nitroaminobenzthiazole formed a yellow solid, which crystallised from alcohol–ethyl acetate in small, yellow plates which charred at 232° (Found : S, 15·9. $C_7H_5O_2N_3S$ requires S, 16·4%). Attempts to brominate this base led only to uncrystallisable bromides.

Bromination of *o*-bromophenylthiocarbamide in chloroform gave rise to a *tribromide* of 3-bromo-1-aminobenzthiazole which crystallised in glistening, orange plates, m. p. 155° (decomp.; charring at 285—290°) [Found : Br, 69·1. $(C_7H_5N_2Br_4S)_2$ requires Br, 68·2%].

In conclusion, the authors desire to express their gratitude to Professors J. F. Thorpe and C. K. Ingold for their interest in this work, and one of them (R. F. H.) is indebted to the Ramsay Memorial Fellowship Trust for a Fellowship awarded to him and also to the Trustees of the Dixon Fund of the University of London for a grant which has helped to defray the cost of some of the materials.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, December 29th*, 1926.]



HEIKE KAMERLINGH ONNES.

[*To face page* 1193.]

Kamerlingh Onnes Memorial Lecture.

DELIVERED ON FEBRUARY 10TH, 1927.

By ERNST COHEN, Hon. D.Sc., Foreign Member R.S.

There can scarcely be a doubt entertained respecting the reducibility of all elastic fluids of whatever kind into liquids; and we ought not to despair of effecting it in low temperatures and by strong pressure exerted upon the unmixed gases.—JOHN DALTON (October, 1801).

An investigator should be almost a monomaniac, possessed of one idea only: to pursue and try to achieve but one purpose, and nothing else. Then, whether he makes a new discovery or not, he will have found satisfaction. But in no other case.—H. KAMERLINGH ONNES.

Je pense que tous ceux qui, en collaboration avec M. ONNES, ont travaillé à Leyde y ont connu des jours heureux.—MADAME CURIE.

LADIES AND GENTLEMEN,—

In 1885 the celebrated Swiss botanist Alphonse de Candolle wrote his enthralling work "Histoire des Sciences et des Savants." He closed one of the chapters of this book—the one in which, with the materials then at his disposal, he indicated to the country of Huygens the place which, about 1870, it occupied in the domain of natural science—with these very reassuring words: "Si mon analyse est vraie, la Hollande se relèvera. L'éclipse actuelle serait momentanée, comme celle de l'Angleterre à la fin du dix-huitième siècle. . . . Il existe encore tant d'excellentes influences en Hollande, qu'on peut espérer raisonnablement un retour de l'ancien éclat scientifique du pays." ("If my analysis is true, Holland will rise again. The actual eclipse is but temporary as the one in England at the end of the 18th century. . . . There are still so many excellent influences in Holland, that one can reasonably hope for a return of the ancient scientific lustre of this country.")

When treating the problems studied by de Candolle, we should now choose other data and criteria, and consequently a new work like de Candolle's is at the present moment a desideratum; but so much is certain, the prophecy pronounced in the sentences quoted has completely come true. This is in no small degree owing to the man whom the Chemical Society elected to its honorary Fellowship in the year 1920, and whom other scientific societies in this country —to mention only the Royal Society and the Royal Institution— honoured with the highest distinctions.

The communications from the Physical Laboratory of the University of Leyden give us a clear insight into what Heike Kamerlingh Onnes has done for science. But the Jubilee Volumes dedicated to him by his friends and co-workers in 1904, in commemoration

of the day when, twenty-five years before, he obtained his Doctor's degree, and in 1922, when he had held his professorate for forty years, are valuable documents in the history of science, which would make a Memorial Lecture superfluous had they not been published in a language which is spoken and read by few only.

Thus the task which has been laid on me becomes a labour of love, because I am allowed to sketch to you the life of my deeply regretted friend, and to recall to your memory some of his great deeds, deeds which signalise him as a man who must be numbered among the " primi inter pares " for all time.

First of all, a few particulars about the period prior to the day (November 11th, 1882) when he was appointed professor at Leyden; we may call this period his youth, for the new professor had not yet attained his thirtieth year. He liked to speak of his youth, of which he always retained the most pleasant memories.

" My father was the owner of a tile factory at Groningen (Heike was born there on September 21st, 1853) and was continually at work to develop his factory and to apply the newest machinery. In his spare hours in the evening he read much and I remember him, sitting before me with his favourite periodical, the *Revue des deux Mondes*. He liked to philosophise and to theorise, and in his walks with us—often with me alone; I was the eldest—many problems were considered and adapted to my level.

" And my mother? When I was sixteen and got up in summer at five o'clock to prepare my school tasks, I often found mother at work in the garden. She had artistic tastes; her father had been an architect.

" My parents had not much intercourse with other people. The business men had different tastes, liked a good dinner, were not averse to a good glass, and talked shop. Among the men of science (Groningen is a university town) my parents had few friends. Therefore we remained at home, read much, talked about art, and developed ourselves consciously, so to say. It was our delight to go for long walks in the country. Sport, as we understand the term now, was hardly known; nowadays for many young people sport is an intentional aim.

" In my parents' house all was made subservient to *one* central purpose: to become *men*. And only when a deep inner culture goes hand in hand with refined good breeding, so that nothing is neglected, and manifests itself also in neat and careful dress, may we expect that the result of such an education will be to form men, in the best and widest acceptation of the word. Has it not been a blessing that I was educated in a family where such ideas obtained? "

In September, 1865, Heike became a pupil of the Hoogere Burger-

school at Groningen, a school which in many respects may be compared to the American High School. The registers of the school relate, not in dry figures, but in glowing terms, that Heike always excelled in zeal, assiduity and knowledge. And also among his school fellows—than whom there are no better judges—the memory lives that Heike was the cleverest pupil of the school. At the time the director was van Bemmelen, later on Professor of Chemistry in the University of Leyden, and Onnes has expressed in feeling terms his gratitude for the influence which van Bemmelen exercised on his pupils.

The school records further tell us : September, 1869, removed to the fifth class (the highest); passes an excellent final examination in 1870; matriculates a short time afterwards to study science at the University.

Our student soon showed that he knew how to combine business with pleasure by joining the Groningsch Studentencorps (Corporation of Students). His club fellows quickly became aware that Heike had completed a great part of his daily task when they had hardly awakened from their sleep. When, in March, 1871, the Utrecht University opened the envelope containing the name of the prizeman to whose essay : " A Critical Investigation of the Methods of Determining Vapour Density and of the Results obtained thereby, with respect to the Relation of the Nature of the Chemical Compounds and the Density of their Vapours," the gold medal had been awarded, the name proved to be

HEIKE KAMERLINGH ONNES
Student in the University of Groningen.

The writer had not yet attained his eighteenth year.

From the way in which the subject matter of this prize essay was treated we see that Onnes was attracted by the study of chemistry, but his inclinations evidenced themselves more clearly after his cand. phys. examination (November 9th, 1871), which he passed with honours; he resolved to leave the country for some time and follow a course of studies with that master-mind in Chemistry who had reaped so many laurels on the banks of the Neckar. So he passed the winter term of 1871 at Heidelberg with Bunsen, the physico-chemist by the grace of God whose humorous sayings were well known to many generations of students and still form the lighter side of the literature of science.

Was it Bunsen's calorimetric investigations, published in 1870, which drove Onnes in 1871 to the birthplace of spectrum analysis? These investigations led to the rediscovery of the ice-calorimeter, which had already been described by Hermann of Moscow in 1834.

Certain it is that our student showed great interest in calorimetric methods in general. This is seen from his essay written in answer to a prize question from the Senate of the State University at Groningen : " A Critical Survey of the Methods of Determining the Quantities of Heat which are set free by Chemical Reactions and Dissociations and of the Results obtained by Different Investigators." Although for this essay Onnes got a silver medal (October 10th, 1872), the opinion of the Senate is not unqualified : " several times serious physical and chemical errors are found," but, on the other hand, it is stated " that he often shows great ingenuity and clever resourcefulness."

Soon we see his inclination for physics cropping out more strongly. At first he worked under the guidance of Bunsen and Kirchhoff; later on, we find him more frequently in the laboratory of Bunsen's friend and co-worker, of the man of whom A. W. von Hofmann said : " Auf meinem langen Lebenspfade bin ich keinem begegnet, bei welchem, wie bei Kirchhoff, höchstes Vollbringen gesellt gewesen wäre mit fast demutsvoller Bescheidenheit." (" During my long life I have never met anyone who, like Kirchhoff, joins the highest power of performance to almost meek humility.")

The " Seminarpreis," awarded to our candidate, which was a great honour, enabled him to work in Kirchhoff's laboratory, a privilege which was granted to two students only. Here Onnes gave himself heart and soul to experiments with Foucault's pendulum, and this investigation became later the starting point for his thesis (" New Proofs for the Axial Changes of the Earth "), which he wrote in his own country. One needs only to glance at the preface of this thesis to see how gratefully the author recalls the time spent at Heidelberg, guided by the man who not only had opened new worlds to mankind, but who had also been endowed with a talent for theoretical and practical investigation, and was a first-rate teacher besides.

Onnes's wanderings ended at the close of his stay at Heidelberg (April, 1873), where Gabriel Lippmann and Arthur Schuster were among his fellow-students. On his return to his native town Professor R. A. Mees became his mentor.

The fact that our student twice obtained the prize for an essay must not lead to the erroneous idea that he belonged to the genus of " plodders." In the Students' Almanacs of the Groningen University mention is made of the fact that Onnes was a very good horseman, and so well liked by his fellow members of the Students' Corporation that they elected him Rector. In their club building, Kamerlingh Onnes's memory is perpetuated by a memorial stone, on which his name is carved, placed there by the gratitude

of his fellow members for the fact that it was especially owing to Onnes's organising talents that the building was brought under direct management. We also read in those annals of students' joy and students' grief that the then Rector took an active part in the movement against a Government measure, at that time under consideration, to abolish the Groningen University.

On June 6th, 1876, Onnes passed his "doctoraal" examination with honours, but the last stage in his academical studies, his Doctor's degree, to be got after he had maintained a thesis, only came a few years later. This is not to be wondered at when we consider the size and the subject of his thesis, which he maintained on Thursday, July 10th, 1879, at Groningen. The Faculty thought its contents and treatment so excellent that they did not require the candidate to leave the room at the end of the examination, as is the custom in Holland, but unanimously and without discussion awarded him the Doctor's degree with great honours (magna cum laude).

When we read the preface of this thesis attentively, we find in it the programme which the young scientist had traced for himself, a programme to which he adhered to the end of his days. "When writing this thesis," he says, "I always tried to take to heart the lesson which the young student in science may find in the Memorial Lecture on Gustav Magnus, written by Helmholtz: 'Gegenwärtig scheint es mir, als wenn immer mehr und mit Recht die Ueberzeugung Boden gewönne, dass in dem entwickelteren Zustande der Wissenschaft nur *derjenige* fruchtbar experimentieren könne, der eine eindringende Kenntnis der Theorie hat und ihr gemäss die rechten Fragen zu stellen und zu verfolgen weiss; und andererseits, dass nur *derjenige* fruchtbar theoretisieren könne, der eine breite praktische Erfahrung im Experiment habe.' ('It seems to me that nowadays the conviction gains ground that in the present advanced stage of scientific investigation only *that* man can experiment with success who has a wide knowledge of theory and knows how to apply it; on the other hand, only *that* man can theorise with success who has a great experience in practical laboratory work.')"

Before taking his doctor's degree, Onnes had fixed his abode in the town where van Leeuwenhoek had lived, and where he filled the post of assistant in Bosscha's laboratory (1878). The four years he spent there were years of hard work; he was required to give Professor Bosscha's course of lectures, and his laboratory work was an excellent training for the future experimenter, as he himself testifies at a later period. The reports of the annals of the students, who were not accustomed to make a secret of their opinions, show us how much his lectures were appreciated by his audience.

A scientist with a career like Onnes's was obviously the right man to fill the vacancy caused by the retirement of Ryke, professor of experimental physics at Leyden. So we see Onnes, on October 11th, 1882, in the Hall of the University, in the chair, to deliver his inaugural lecture in which he sketched the importance of quantitative investigation in physics. This day was the beginning of a new period in his life, but it was also for Onnes the dawn of his triumphal progress through the realm of low temperatures.

Time is lacking to describe this triumphal progress in detail. But for one short moment I wish to dwell on the above-mentioned lecture of 1882 and on the one delivered by Onnes as " Rector Magnificus " of the University of Leyden : " The Importance of Accurate Measurements at very Low Temperatures." Even at the present day these addresses have a great fascination for the reader. We do not know which excites our admiration more : his prophetic eye or the unequalled energy he displayed at a ripe age in accomplishing the programme he had at one time evolved. If we want completely to understand the contents of these addresses, we must first of all try to realise the progress of physics, especially of thermodynamics, about 1875.

Two years earlier a man had obtained his doctor's degree at Leyden, after maintaining a thesis : " On the Continuity of the Gaseous and Liquid States," whose work elicited a year later the remark of Clerk Maxwell (in a lecture delivered to this Society on February 18th, 1875) : " . . . but his attack in this difficult question is so able and brave that it cannot fail to give a notable impulse to molecular science. It certainly has directed the attention of more than one inquirer to the study of the Low-Dutch language in which it is written."

We know now, from a letter from Andrews at Belfast to James Thomson (February 5th, 1874), that this view was correct : " P. S. Bessie and I are hard at work on Diderik van der Waals," and a few months later Andrews writes : " My dear Thomson. . . . I am deep in the Dutch paper and also occupied with my own results, which I believe will turn out more important than I supposed. But I miss you sadly."

Fourteen years later the paper of van der Waals was translated into English under the auspices of the Physical Society in London.

The experimental testing of the equation of state, given by van der Waals in his thesis, together with the one of the law of corresponding states, published by van der Waals in 1880, formed the first part of Onnes's programme.

In later years he tells us : " This law had a special charm for me, because I was of opinion that it was based upon the stationary

mechanical similitude of the substances considered. From this point of view the study of the divergences in substances of simple chemical structure with low critical temperature seemed to me of great importance. Precision measurements at low temperature must be very attractive in my opinion. For this purpose, it was necessary to dispose of large apparatus with which the measurements could be made at a constant temperature, and it was indispensable to construct suitable temperature baths, baths which could also be used for numerous other investigations."

Thus, as soon as Onnes had entered upon his new sphere of activity, the foundations were laid of an institution in which the investigations in question could be taken in hand—the Cryogenic Laboratory of Leyden, which, in consequence of the results attained, was soon to become an international centre of research.

The efforts of Onnes and his co-workers met with stupendous success. In 1904 liquefied air and oxygen formed the boundary line of the low temperatures which could be obtained with cryostats; two years later hydrogen could be made in large quantities. Eight years before, Dewar had liquefied this gas in the laboratory of the Royal Institution in this city. The reason why so much time elapsed between the moment when Dewar could wire to Onnes: "Hydrogen liquefied," and the application at Leyden was that Onnes wanted to have at his disposal large quantities of liquids for his cryostats.

When we read the papers on the investigations in the Leyden Laboratory we are struck again and again by the great appreciation which Onnes had for the men who were working in the domain which he had chosen for his life-work, and he continually admits that he owes much to their researches. In his address of 1904 he says: "In the meantime, an entirely new path has been struck by Dewar with respect to investigations at low temperatures. He taught us to make glass vessels, beakers, bulbs, and glasses in which liquids with boiling points at very low temperatures could be kept and transported. These vacuum vessels have double walls which are silvered on the inside, whilst the space between them is exhausted to the utmost. The access of heat from without is now diminished to such a degree that the liquid does not evaporate perceptibly. By means of this invention we gained the desired free disposal of refrigerants like liquid oxygen. Dewar's magnificent invention may be called the most important appliance for operating at extremely low temperatures. The open vacuum flasks are for the permanent gases what the steel bottles, tested at 250 atmospheres, are for the coercible gases. In fact, the moment when a vacuum glass containing liquid oxygen was offered to the Prince of Wales at the meeting

of the Royal Institution marks a new era in low-temperature research."

The words which Henry E. Armstrong used in his most fascinating address dedicated to the memory of James Dewar may be unconditionally applied to Onnes : " His object was never merely to liquefy gases. He was never the mere artificer, but always the philosopher seeking to penetrate into the far distant region of the ultimate zero of temperature." This very fact made Onnes's creation at Leyden the place where investigators from all parts of the world could carry on their research work. Thus this building, distant but a few steps from the spot where, two centuries before, Boerhaave had expounded to his students Boyle's " Experimental History of Cold," became the place where physics in their entirety, physical chemistry, physiology, could be studied at the lowest point of temperature.

" Wer zählt die Völker, nennt die Namen,
Die gastlich hier zusammen kamen ? "

(" Who counts the nations or knows the names of all who were hospitably received here ? ")

These words of the poet would make a suitable inscription, not only for the Cryogenic Laboratory, but also for Onnes's artistic house, where so many scientists could and did find relaxation from their strenuous labours.

Science owes much to Lavoisier's wife for the share she took in her husband's work, but no less praise is due to Elisabeth Byleveld, who, since September, 1887, shared the sweets and bitters of Onnes's life. Besides her duties as a mother, which she fulfilled with the greatest tenderness, she always guarded her husband from the troubles of daily life as much as lay in her power and she took the greatest care of his ailing health. Onnes himself says : " She has toiled for me, has always been ready to put her own wishes in the background, has received my guests, and taken care of them."

All who have stayed in her hospitable home know that when her husband had finished his daily task in the hyper-arctic regions of science, he found in her companionship the warmth necessary to stimulate his energy for new problems. And new achievements were not wanting, even up to the last days of Onnes's life; the unending flow of communications from the physical laboratory of the University of Leyden testifies this. In these communications are the results of thermodynamic, magnetic, magneto-optical, radioactive and electric investigations at the lowest temperatures. In this hour I recall to your memory one of the most remarkable and far-reaching achievements of Onnes and his staff, the one which

more than any other entitles him to the epithet of " gentleman du zéro absolu." The day is December 10th, 1913, the anniversary of the death of Alfred Nobel. A select crowd has met in the Great Hall of the Royal Academy of Music at Stockholm, where those to whom Nobel prizes have been awarded are to receive the insignia from the hands of the King of Sweden. As is seen from the following lines, Onnes is among the laurelled :

HEIKE

KAMERLINGH ONNES

for hans undersökningar öfver kroppars egenskaper vid läga temperaturer hvilka bland annat ledt till framställningen af flytande helium.

Stockholm den 10 December 1913.

TH. NORDSTRÖM,
Kungl. Vet. Akad-s preses.

CHR. AURIVILLIUS,
Kungl. Vet. Akad-s sekreterare.

(For his investigations on the properties of substances at low temperatures, which investigations, among other things, have led to the liquefaction of helium.)

The next day he mounted the platform and sketched the " Leiden und Freuden " (disappointments and joys) of the years that lay behind him. After pointing out that the theories of van der Waals and more particularly his " law of corresponding states " had guided him, he surveys the results attained by Wroblewsky, Olszewski, Pictet, Linde, and Dewar at low temperatures, and in imagination he leads his audience through the Leyden Cryogenic Laboratory. He introduces them to his numerous co-workers, among whom Crommelin has especially distinguished himself in the technical part of the work, and finally depicts to them the way in which helium was liquefied : " The limit of what was possible was reached, as had been foreseen when the plans were formed. The experiment (July 10th, 1908) began at half past six a.m. and ended at half past nine p.m. When at half past six p.m. the first liquefied helium was perceived, not only had the apparatus been strained to the uttermost, but the utmost had also been demanded from my assistants. But for their perseverance and their ardent devotion, every item of the programme would never have been attended to with such perfect accuracy as was necessary to render this attack on helium successful. In particular I wish to express my great indebtedness to Mr. G. J. Flim, who, as chief of the technical department of the Cryogenic Laboratory, not only assisted me in

leading the operations, but also superintended the construction of the apparatus according to my direction and rendered me the most intelligent help in both respects.

"It was a wonderful moment when the liquid, which looked almost immaterial, was seen for the first time. It had not been perceived when it flowed into the glass; its presence could be detected only when the glass had been filled. Its surface stood out sharply defined like the edge of a knife against the glass wall. I was overjoyed when I could show liquefied helium to my friend van der Waals, whose theory had been my guide in the liquefaction up to the end."

And when, later on, Onnes himself relates that on this memorable day his wife fed him, beginning at three o'clock, by putting bits of bread into his mouth, there rises up before us the image of Caroline Herschel, your compatriot, who read to her brother, Sir William, when he was polishing his mirrors, and—to use her own words—" was constantly obliged to feed him by putting the victuals by bits into his mouth."

But, Ladies and Gentlemen, read the "Communications" for yourselves; the description of the journey to the nadir of temperature, and especially the famous discovery by Onnes (1913) of the supra-conductivity of metals at very low temperatures, will awaken your interest as much as the most thrilling novel. According to the electron gas theory of metallic conduction, one might have expected that the resistance of a metal would diminish continuously with fall of temperature, or even that the resistance at very low temperatures might begin to rise sharply, owing to a sort of freezing of the electrons. Onnes made the startling discovery that the resistance of certain metals suddenly falls to zero (or to an extremely low value, at a temperature varying with the nature of the metal) a few degrees above the Kelvin zero point.

Even before the verdict of the scientific world had assigned the Nobel prize to Onnes, Dutch scientists had given him a token of their profound veneration. Not one of the numerous company which had gathered in the Great Hall of the Amsterdam University on November 18th, 1908, on the occasion of the Annual General Meeting of the Ancient Association of Physics, Medicine, and Surgery, but will think with emotion of an event in the history of science at which he was then assisting. For on that day van der Waals and Kamerlingh Onnes were to be given a mark of the high appreciation which was felt by the whole scientific world; to each of them was to be presented the medal of honour, the highest mark of distinction at the disposal of the Association, to Onnes for the

liquefaction of helium, to van der Waals for his "law of corresponding states."

"Expressed in mathematical terms," thus van der Waals addressed Onnes, "this law may be formulated in this way: If we consider different substances at temperatures which are an equal number of times their critical temperatures, and under pressures which are an equal number of times their critical pressures, the volumes are each an equal number of times the critical volume.

"Elsewhere I have expressed this differently, in words that can be more easily understood: all substances form one single genus. If we compare, for instance, height with temperature, breadth with pressure, and length with volume, we can say that all substances are copies of one another. If one substance has a critical point, such a point must appear in all the others. But whereas, in individuals belonging to the same genus, the differences in height, breadth, and length are but slight, these differences may be very great with temperature in the different substances. Thus the critical temperatures sometimes diverge in the proportion of 1 to 1000.

"Now it was a question whether helium, the discovery of which has taken place in recent years only, also belongs to this common genus, whether this dwarf also has a well-formed shape. We owe it to you, highly esteemed Kamerlingh Onnes, that now we know this for certain. Only you could investigate it in your cryogenic laboratory, which is unequalled for organisation. You conducted this investigation systematically. By carrying out measurements of pressure and volume at the lowest possible temperature, you were able to determine the so-called Boyle point, *i.e.*, the temperature at which, with very great volume, the substance follows Boyle's law. For all substances, the Boyle point is rather more than three times higher than the critical temperature, according to the equation of state 27/8 times the critical temperature.

"Strictly speaking, the question was now settled: Helium too possesses this very same remarkable point; moreover, the critical temperature of helium, being rather more than three times lower than the Boyle point, was also known. Dewar had already announced that helium has a reversion temperature for the Joule–Kelvin effect. But this lies rather more than six times higher than the critical temperature. So you had halved the distance which separated actual results from the critical temperature of helium. But you would not stop here; you wanted to see not only the front and face of the well-formed shape, but its heart also. You wanted to reach the critical temperature itself and to liquefy the substance. And on the memorable 10th of July, after a long day's

work, surrounded by a staff of well-trained observers, you achieved it after careful preparation.

" First of all, you deduced, from the value found for the Boyle point, that the critical point would lie about 6° above absolute zero. Then, assuming the well-formed shape, you calculated how much helium you would require, considering the size of your apparatus, to what temperature you would have to cool it at first by means of hydrogen, and to what pressure you would have to submit it, so that by free expansion it could cool itself to below 6°. Having considered everything, you worked the summer day through, until, long after sunset, you succeeded in liquefying helium. You have made it possible to approach much closer to the absolute zero than could be done up to this time, an achievement which is of the highest importance for many scientific problems in which the influence of low temperatures has to be studied.

" It is therefore with a feeling of admiration for the results you have attained, with a feeling of veneration for your character as a man and an investigator, with a feeling of gratitude on account of science in Holland—because, as Korteweg said at the Royal Academy of Sciences, you have made the heart of every Dutch scientist thrill with joy and with a feeling of warm friendship—that I present to you this commemorative medal in the name of the Association for the Advancement of Physics, Medicine, and Surgery."

Van der Waals spoke a true word when he gave utterance to his feelings of veneration for Onnes's character as a man and an investigator. An incident in the previous history of the liquefaction of helium proves this, an incident which should serve as an example for all scientists : On March 5th, 1908, Onnes wired to Dewar in London : " Converted helium into solid. Last evaporating parts show considerable vapour pressure, as if liquid state is jumped over." On April 16th, Onnes wrote to the editor of *Nature* : " . . . The prosecution of the experiments has shown that what I observed in expanding the gas was *not* the evaporation of *solid* helium, but solution phenomena of solid hydrogen in gaseous helium. I have communicated to the Amsterdam Academy a note on my experiments, which at the moment leave the condensation of helium a yet undecided question." With unflagging zeal Onnes set to work again : on July 10th of the same year the problem was solved : helium had been liquefied.

The results attained could not but stimulate our untiring investigator to new labours. First and last his maxim is " *Inferior !* "

In a paper " On the Lowest Temperature yet obtained. An Introductory Paper to a General Discussion on the Generation and

Utilisation of Cold," read before the Faraday Society and the British Cold Storage and Ice Association on Monday, October 16th, 1922 (proof subject to revision), he summarised his newest conquests in the words : " Taking into account the uncertainty of the extrapolation, it will be better to say that the lowest temperature yet attained is some hundredths of a degree below 0·9K."

Onnes was obliged to leave the last stage of the work on which he had set his heart, the solidifying of helium, to one of his most brilliant pupils, whom he also recommended as his successor. At least five times (for the first time in 1908) Onnes tried to attain the result, but he never succeeded. Only a few months after his death (he passed away on February 21st, 1926) this refractory substance was subjugated by Keesom.

The plans which Onnes had already formed when he became professor at Leyden and grew to greater proportions as his work progressed (" Es wächst der Mensch mit seinen grössern Zwecken " . . . man grows with his growing projects . . .) required, not only a talented experimenter, but also a man with great organising ability. And Onnes had been gifted in this respect also. As such he rendered an invaluable service to the craft of instrument-making by founding the Society for the Promotion of the Training of Instrument-makers (1901). He gave new life to the traditions which arose in the workshop of van Mussenbroek Brothers at Leyden as early as the 17th century. Scientists constantly demand better instruments by means of which they can penetrate into the heart of Nature, and consequently greater demands are made on the makers of these appliances. Onnes's training school for instrument-makers, annexed to the Cryogenic Laboratory, was not only a training school for his own mechanics by which he was enabled to surmount many difficulties that presented themselves in his investigations; it became an establishment at which the laboratories in Holland have an excellent opportunity of providing themselves with first-rate workmen, and which has given many an excellent instrument-maker to the laboratories in Europe as well as to institutions beyond the Atlantic.

From what I have told you about Onnes's work you must have gathered that what he accomplished may be considered a stupendous achievement even for a man in normal health. Such a task is the more remarkable because Onnes had always to contend with his bronchial weakness. It is sad to read in the letters which he wrote from time to time to his friend van der Waals how much he was handicapped by his weak health, but the indomitable energy which urged him on to new problems awakens our admiration. Notwithstanding these reverses, which often retarded the progress of his

work, he was always happy. To van der Waals he wrote on September 11th, 1912, a few days after his silver wedding :

LEYDEN, *Sept.* 11*th*, 1912.
HUIZE TER WETERING.
HAAGWEG.

" DEAR FRIEND,—We deeply regretted that you could not come to Leyden yesterday as we had so much hoped. We should have liked to thank you in person for the kind letter, written in the name of all of you, and for the fine flowers with which you added lustre to our reception. For the time being, our room was a flower garden for the bride at her silver wedding.

" Our silver wedding was an event the commemoration of which had for a long time been looked forward to as a day which would fill us with heartfelt thankfulness for the many blessings we had received in the twenty-five years which lie behind us. So you will understand that we celebrated this day with thankful hearts and that we shall always look upon it as a pleasant milestone on the road which lies behind us.

" Which of us, Betsy,* Albert,† or myself, was most affected by these feelings is hard to say. All of us are equally conscious that our gratitude can never be great enough for the supreme happiness and prosperity which have been showered upon us. As for the prosperity, the measure of it can be realised best by me, because after our marriage the cares which I had known before diminished. When I re-read mother's letters, written in those most care-ridden years, it is as if I look back upon a totally different world, and it seems to me that only now I realise how appalling were the difficulties with which we had to contend—always hopefully after mother's example—until at last they gave way. When I think of that time, our present prosperity makes me doubly thankful. And as for the happiness we enjoy, although it has been mixed with affliction—the sad loss of our parents is still a source of sorrow—we have been favoured above many, because we have been allowed to possess them for so long a time in mutual love. And while gratefully accepting all this abundant happiness, a feeling of modesty and diffidence comes over us. When we thought of our future we felt the need of lifting up our hearts, and therefore we were deeply moved when Albert, who executed the recitative, and Harm ‡ with the two nieces who accompanied, received us at breakfast in the family circle of brothers and sisters with a solemn aubade.

* His wife. † His son. ‡ His nephew.

"May your wish 'that we shall long be spared for each other, every one of us labouring to the best of his ability'—which is also our fervent hope—be fulfilled. Once more our best thanks, with cordial greetings from all to all. In the name of our old friendship,

Cordially yours,
H. KAMERLINGH ONNES."

All who realised the important part which nowadays is played by temperatures below freezing point welcomed with satisfaction the co-operation between technics and science which was brought about by the institution of the "Association internationale du Froid" (1909), in which Onnes also took an active part. About ten years later it was reconstructed under the name of "Institut international du Froid." It was there that for the first time the epithet of "gentleman du zéro absolu" was applied to Onnes, whilst in his own country his popularity appears from a cartoon in which he is given the sobriquet of the "Freezer." Whoever reads the annual reports of the "Institut international du Froid" will agree that, contrary to the prevailing idea, low temperature had not impaired Onnes's energy and rate of reaction when it was necessary to promote the interests of the Institute. Is it to be wondered at that numerous learned Societies in his country and abroad, borrowing Saurin's line under the bust of Molière :

"Rien ne manque à sa gloire, il manquait à la nôtre"

have awarded their highest distinctions to Onnes. This was done also by this Society. He valued such marks of distinction very much, as may be seen from a passage in a letter to his friend van der Waals, in which he congratulates him on his election as corresponding member of the French and Prussian Academy of Sciences. Onnes says : "... the proof that slowly your work is being understood must be a source of great satisfaction to you."

At the commencement of my discourse I mentioned the beautiful international Jubilee volume which was presented to Onnes on November 11th, 1922, on the occasion of the fortieth anniversary of his professorate. On that memorable day all vied with one another as to who should be the first to show him, beside appreciation of his scientific labours, admiration for his amiability which had engendered love in the hearts of all who made his acquaintance. The staff of his laboratory, too, wished to give expression to their feelings. When visiting the Cryogenic Laboratory at Leyden, you

will notice a memorial stone of grey marble, in which are carved these words :

> " On this spot, on the 10th of July, 1908, Helium was liquefied for the first time by Dr. HEIKE KAMERLINGH ONNES.
>
> The entire staff of the laboratory has presented to him this memorial on the occasion of the 40th anniversary of his professorate.
>
> November 11th, 1922."

On this festal day an amazed audience admired the rare phenomenon of a fountain of liquid air. And, while reminding you of that day, I must not omit to mention the words spoken by Onnes about the cordial relations that existed between him and H. A. Lorentz :

" Now that I am speaking about friendship," thus he said, " I also think of my older friend Lorentz. We began our studies at the same time, and I can glory in a friendship of more than fifty years, a friendship which was shared by our mutual households. It has always been a great privilege to work with such a man as Lorentz. First he preserved my health by giving several of my lectures, which had the additional advantage of allowing me more time for my work in the laboratory. And later on, when he was called to Munich, it was by his efforts that Kuenen came here, who, as I have said before, succeeded in making the laboratory for the greater part what it actually is."

It is as if I still hear his voice when, on February 8th of last year, one day before my departure for America, he telephoned to me, wishing me a prosperous voyage and expressing the hope to see me again in good health on my return. Fortunately, he was spared a long sick bed; no sooner had I set foot ashore on the other side of the Atlantic than the sad tidings of his death reached me.

When we see how scarce really noble characters are among the living, and, on the contrary, how plentiful among the dead, according to biographies and epitaphs, we cannot wonder that the world in general refuses to believe in the existence of such characters, either among the living or the dead. And yet in Kamerlingh Onnes we had a man in whom it is difficult to discover qualities which one would have wished different. He was not only the " gentleman du zéro absolu," but, as my friend Donnan has said, " a gentleman in every sense of the word, and one of the first gentlemen of European science."

Thus Kamerlingh Onnes has lived his life—a life, although long, yet too short for my friend himself, too short for his family, too short for science. Many blessings fell to his lot and, although grief was not spared him, the benefits prevailed. He found love and friendship; he had an intellectual life, rich in discoveries, as is given but to few. Love, friendship, discoveries, and also honour. For Kamerlingh Onnes was not one of those whose merits are recognised at a ripe age only. He was an unknown scholar for but a short number of years. Very soon his life became one triumphal progress. And is it not his greatest triumph that in spite of all the marks of esteem which were showered upon him by all the world he remained a simple, genial, and kind-hearted man.

CLXV.—*Aminobenzthiazoles. Part IX. The Unsaturation of Aminobenzthiazoles containing a Static Triad System, and the Synthesis of some* 1-*Dimethylaminobenzthiazoles.*

By Robert Fergus Hunter and Eric Rofe Styles.

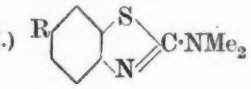
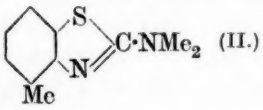
It has been suggested (Hunter, J., 1926, 1385; Hunter and Soyka, *ibid.*, p. 2959) that the production of isomeric bromides from aminothiazoles containing a mobile amidine system [H]N·C:N ⇌ N:C·N[H] is due to the addition of bromine to the tautomeric forms of the triad system. It being obviously desirable, therefore, to examine static derivatives (I) in which both mobile hydrogen atoms have been alkylated, the bromination of certain *s*-aryldimethylthiocarbamides and 1-dimethylaminobenzthiazoles was undertaken.

On bromination in chloroform, *s*-phenyldimethylthiocarbamide readily gave a *dibromide* of 1-dimethylaminobenzthiazole, which yielded the dimethylaminobenzthiazole (I; R = H) on reduction in the usual way (*loc. cit.*). A well-defined *pentabromide* of the dimethylamino-base was sometimes isolated, which was probably the hydrobromide of the tetrabromo-addition compound of the base. The bromination of *s*-phenyldimethylthiocarbamide, however, proceeded less readily than that of phenylthiocarbamide and of *s*-phenylmethylthiocarbamide (J., 1926, 1385), and this is probably due to the fact that in phenylthiocarbamide the mobile triad system [H]N·C:S ⇌ N:C·S[H] is duplicated in such a way as to favour the production of the thioamide phase of the thiocarbamide, through which thiazole ring formation takes place by way of a labile ·CBr–SBr derivative (Hunter and Soyka, *loc. cit.*). In any case, some *s*-phenyldimethylthiocarbamide was recovered un-

changed under conditions in which phenylthiocarbamide was completely transformed into 1-aminobenzthiazole dibromide.

On bromination in chloroform with excess of bromine, 1-*dimethylaminobenzthiazole* readily yielded a well-defined *hexabromide* (compare Hunter, J., 1925, **127**, 2271, and later papers).

The bromination of s-o-*tolyldimethylthiocarbamide*, however, gave rise to a well-defined, stable *tetrabromide* of 1-dimethylamino-3-methylbenzthiazole, which yielded the 3-methyl base (II) on

(I.)  (II.) 

reduction in the usual way. This tetrabromide only lost bromine on exposure to moist air for several weeks, and it must be assumed that the instability produced in the NBr_2 complex by the *o*-methyl group (Hunter, J., 1926, 1401) is more than neutralised in the presence of the μ-NMe_2 group. This suggested that the bromides of the 5-substituted 1-aminobenzthiazole bases prepared by Dyson, Hunter, and Morris (preceding paper) might be greatly stabilised, and thereby rendered more readily comparable, by dimethylation of the amino-group, and the bromides of the 5-substituted 1-dimethylaminobenzthiazole bases (I) were therefore studied. In every case, bromination of the *s-p*-substituted phenyldimethylthiocarbamide gave rise to the bromide of the corresponding dimethylaminobenzthiazole, and these compounds differed strikingly from the bromo-addition compounds described in the preceding paper as regards their stability to moist air; on reduction, they all yielded the corresponding 5-substituted bases (I) in the usual way.

s-p-*Methoxy-* and s-p-*ethoxy-phenyldimethylthiocarbamide* yielded the tetrabromides of 5-methoxy- and 5-ethoxy-1-dimethylaminobenzthiazole, respectively. p-*Tolyldimethylthiocarbamide* resembled phenyldimethylthiocarbamide and gave rise to a *pentabromide* of 1-dimethylamino-5-methylbenzthiazole, which was very probably the hydrobromide of the tetrabromide. Bromination of 1-dimethylamino-5-methylbenzthiazole (I; R = Me) gave rise to a *hexabromide* of this base. p-*Chlorophenylthiocarbamide*, however, on bromination under the usual conditions yielded a *tribromide* of 5-chloro-1-dimethylaminobenzthiazole which was probably the hydrobromide of the dibromo-addition compound of the 5-chloro-base.

In view of the alternation of hexabromides and tetrabromides in the ascending homologous series of 2-alkylamino-β-naphthathiazole bromides (Dyson, Hunter, and Soyka, J., 1926, 2965), the bromination of s-α-*naphthyldimethylthiocarbamide* was also

studied. As might have been anticipated, this thiocarbamide gave rise to the tetrabromo-addition compound of the naphthathiazole, which yielded 2-*dimethylamino*-β-*naphthathiazole* on reduction.

Experimental.

The *s*-aryldimethylthiocarbamides described below were prepared, in yields of 80—90%, by treating the arylthiocarbimides (preceding paper) (1 mol.) in alcohol (5 vols.) with a 20% excess of a 33% solution of dimethylamine in absolute alcohol; in each case the mixture was warmed, and then concentrated at 15°/20 mm. The thiocarbamides were usually recrystallised from absolute alcohol.

s-Phenyldimethylthiocarbamide crystallised in long prisms, m. p. 133° (compare Dixon, J., 1892, **61**, 539) (Found: S, 17·6. Calc.: S, 17·8%).

1-*Dimethylaminobenzthiazole Dibromide*.—A solution of phenyldimethylthiocarbamide (1 g.) in chloroform (10 c.c.) was slowly treated with 0·8 c.c. of bromine; a yellow precipitate (bromo-addition compound of the thiocarbamide?) formed, which redissolved with evolution of heat and hydrogen bromide. The mixture was refluxed for 5 minutes and concentrated. It could not be induced to crystallise * and therefore was evaporated in a vacuum at 15°. The red gum obtained, after remaining in an evacuated desiccator for 20 hours, solidified in small, hard, vermilion crystals of the *dibromide*; these, after being crushed on porous earthenware and dried in a vacuum over potassium hydroxide, melted at 91—93° (decomp.; reddening at 60—70°, softening at 75—80°) (Found: Br, 48·0. $C_9H_{10}N_2Br_2S$ requires Br, 47·3%). This compound had the usual properties and liberated iodine from dilute hydriodic acid (Found: Br, 40%).

1-*Dimethylaminobenzthiazole tetrabromide hydrobromide* (prepared from phenyldimethylthiocarbamide, 2 g.; chloroform, 20 c.c.; bromine, 2 c.c., in chloroform, 5 c.c.; time of refluxing, 15 minutes) separated, after the mixture had been concentrated in a vacuum at 15°/20 mm., in small, orange-red prisms, m. p. 101° (decomp.) after drying (Found: Br, 69·1. $C_9H_{10}N_2Br_4S,HBr$ requires Br, 69·1%).

1-*Dimethylaminobenzthiazole*.—Either of the preceding bromides was treated with a large volume of sulphurous acid (saturated with sulphur dioxide at 15°) and the filtrate therefrom was made strongly alkaline with ammonia (*d* 0·880); the base then crystallised in glistening flakes, m. p. 86°. After recrystallisation from alcohol

* After this bromide had once been obtained crystalline, there was no difficulty in inducing subsequent preparations, made in the same laboratory, to crystallise.

it formed small, glistening needles, m. p. 87° (Found : S, 17·7. $C_9H_{10}N_2S$ requires S, 18·0%).

1-*Dimethylaminobenzthiazole hexabromide* (prepared from dimethylaminobenzthiazole, 0·8 g.; chloroform, 15 c.c.; bromine, 1 c.c.) separated in orange-red, glistening plates, m. p. 211° (with efferv.) after being dried (Found : Br, 73·2. $C_9H_{10}N_2Br_6S$ requires Br, 73·0%).

s-o-*Tolyldimethylthiocarbamide* crystallises in shining prisms, m. p. 138° (Found : S, 16·3. $C_{10}H_{14}N_2S$ requires S, 16·5%).

1-*Dimethylamino*-3-*methylbenzthiazole tetrabromide* (prepared from *o*-tolyldimethylthiocarbamide, 2 g.; chloroform, 10 c.c.; bromine, 2 c.c., in 5 c.c. of chloroform; spontaneous boiling with evolution of hydrogen bromide; time of refluxing, 10 minutes) crystallised in orange-yellow, glistening prisms, which after drying had m. p. 160° (decomp.; softening at 125—130°, charring at 180°) (Found : Br, 62·3. $C_{10}H_{12}N_2Br_4S$ requires Br, 62·5%).

1-*Dimethylamino*-3-*methylbenzthiazole* was obtained by reduction of the tetrabromide with a large volume of sulphurous acid, and crystallised from alcohol in stellate clusters of glistening needles, m. p. 84° (Found : S, 16·4. $C_{10}H_{12}N_2S$ requires S, 16·7%).

s-p-*Methoxyphenyldimethylthiocarbamide* crystallised in glistening plates, m. p. 125° (Found : S, 15·3. $C_{10}H_{14}ON_2S$ requires S, 15·2%).

1-*Dimethylamino*-5-*methoxybenzthiazole tetrabromide*, obtained from 0·9 g. of *p*-methoxyphenyldimethylthiocarbamide in chloroform (6 c.c.) and bromine (0·9 c.c.), formed small, yellowish-orange plates, m. p. 195° (with efferv.) (Found : Br, 61·1. $C_{10}H_{12}ON_2Br_4S$ requires Br, 60·6%).

1-*Dimethylamino*-5-*methoxybenzthiazole* crystallised from alcohol in small, white prisms, m. p. 144° (Found : S, 15·1. $C_{10}H_{12}ON_2S$ requires S, 15·4%).

s-p-*Ethoxyphenyldimethylthiocarbamide* formed small, shining prisms, m. p. 163° (Found : S, 14·2. $C_{11}H_{16}ON_2S$ requires S, 14·3%).

1-*Dimethylamino*-5-*ethoxybenzthiazole tetrabromide* (prepared from the ethoxyphenyldimethylthiocarbamide, 1 g.; chloroform, 10 c.c.; bromine, 1 c.c.; time of refluxing, 2 minutes) separated in orange, glistening plates, m. p. 190° (decomp.) (Found : Br, 59·0. $C_{11}H_{14}ON_2Br_4S$ requires Br, 59·1%).

1-*Dimethylamino*-5-*ethoxybenzthiazole* crystallised in small prisms, m. p. 118° (Found : S, 14·1. $C_{11}H_{14}ON_2S$ requires S, 14·4%).

s-p-*Tolyldimethylthiocarbamide* crystallised in glistening plates, m. p. 169° (Found : S, 16·1%).

1-*Dimethylamino*-5-*methylbenzthiazole tetrabromide hydrobromide* was obtained from *p*-tolyldimethylthiocarbamide (2 g.) in chloro-

form (15 c.c.) and bromine (2 c.c.). After the mixture had been refluxed, and then concentrated in a vacuum for 2 minutes, the product crystallised in glistening, orange-red needles, m. p. 95° (decomp.; efferv. at 125°) (Found: Br, 67·8. $C_{10}H_{12}N_2Br_4S,HBr$ requires Br, 67·6%).

1-*Dimethylamino*-5-*methylbenzthiazole* separated from alcohol in small, glistening prisms, m. p. 86° (Found: S, 16·3%).

1-*Dimethylamino*-5-*methylbenzthiazole Hexabromide*.—One c.c. of bromine in chloroform (5 c.c.) was added to a solution of 0·9 g. of 1-dimethylamino-5-methylbenzthiazole in chloroform (15 c.c.); the hexabromide then separated in orange-red, glistening plates, m. p. 188° (decomp.) (Found: Br, 72·0. $C_{10}H_{12}N_2Br_6S$ requires Br, 71·4%).

s-p-*Chlorophenyldimethylthiocarbamide* formed small prisms, m. p. 152° (Found: S, 14·6. $C_9H_{11}N_2ClS$ requires S, 14·9%).

5-*Chloro*-1-*dimethylaminobenzthiazole dibromide hydrobromide*, obtained from 0·6 g. of *p*-chlorophenyldimethylthiocarbamide, suspended in chloroform (4 c.c.), and bromine (0·6 c.c.), crystallised in aggregates of orange-yellow needles, m. p. 264° (decomp.; sintering at 190°) (Found: Br, 54·6. $C_9H_9N_2ClBr_2S,HBr$ requires Br, 52·9%).

5-*Chloro*-1-*dimethylaminobenzthiazole* crystallised from alcohol in long, colourless prisms, m. p. 99° (Found: S, 15·0. $C_9H_9N_2ClS$ requires S, 15·1%).

s-α-*Naphthyldimethylthiocarbamide* crystallised in long prisms, m. p. 162° (Found: S, 13·8. $C_{13}H_{14}N_2S$ requires S, 13·9%).

2-*Dimethylamino*-β-*naphthathiazole tetrabromide* was prepared from the naphthyldimethylthiocarbamide (0·3 g.) in chloroform (3 c.c.) and bromine (0·3 c.c.) and formed a bright yellow, crystalline powder which sintered at 185° and melted at 225° (decomp. with charring) (Found: Br, 58·3. $C_{13}H_{12}N_2Br_4S$ requires Br, 58·4%).

2-*Dimethylamino*-β-*naphthathiazole* crystallised from alcohol in large, flat prisms having a yellow tinge; m. p. 138° (Found: S, 13·9. $C_{13}H_{12}N_2S$ requires S, 14·0%).

In conclusion, the authors desire to express their gratitude to Professor J. F. Thorpe, F.R.S., for his interest in these experiments, and one of them (R.F.H.) is indebted to the Ramsay Memorial Fellowship Trust for a Fellowship and to the Dixon Fund of the University of London for a grant which has defrayed the cost of some of the materials used in this work.

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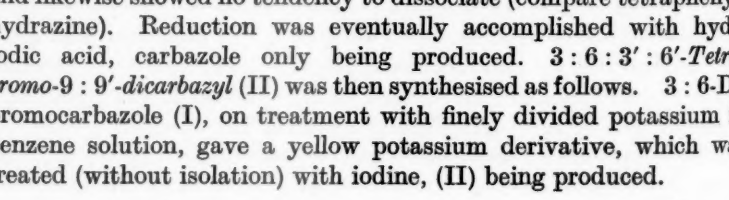
CLXVI.—*The Dicarbazyls. Part II. 9 : 9′-Dicarbazyl and its Halogen Derivatives.*

By JOHN McLINTOCK and STANLEY HORWOOD TUCKER.

WIELAND and GAMBARJAN (*Ber.*, 1906, **39**, 1506) have stated that no bisdiphenylenehydrazine (9 : 9′-dicarbazyl) is produced when carbazole is treated with lead peroxide in benzene or with potassium permanganate in cold acetone, although both of these reagents act on diphenylamine giving tetraphenylhydrazine. Later, Perkin and Tucker (J., 1921, **119**, 216) obtained two crystalline dicarbazyls, A and B, and an amorphous product, C, by oxidising carbazole with potassium permanganate in hot acetone. The hydrogen atoms in the 9- and 3-positions of the carbazole molecule are the most reactive, and migration of groups from the 9- to the 3-position is common. Any method, therefore, which will prevent oxidation at one or other of these positions will tend to reduce the number and complexity of the oxidation products. It was with this idea in view that we attempted the oxidation of 3 : 6-dihalogen derivatives of carbazole, in the hope that oxidation would be confined to the imino-group.

When 3 : 6-dibromocarbazole was oxidised by the method of Perkin and Tucker (*loc. cit.*), a tetrabromodicarbazyl was produced. It was expected that, if this were a 9 : 9′-dicarbazyl derivative, it would reduce with comparative ease to 3 : 6-dibromocarbazole. The substance was very stable towards reducing agents, however, and likewise showed no tendency to dissociate (compare tetraphenylhydrazine). Reduction was eventually accomplished with hydriodic acid, carbazole only being produced. 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl* (II) was then synthesised as follows. 3 : 6-Dibromocarbazole (I), on treatment with finely divided potassium in benzene solution, gave a yellow potassium derivative, which was treated (without isolation) with iodine, (II) being produced.



(I.) (II.)

The oxidation product of 3 : 6-dibromocarbazole was found to be identical with (II).

Following on this, the first recorded synthesis of a derivative of 9 : 9′-dicarbazyl, we made attempts to isolate the unsubstituted hydrazine (9 : 9′-dicarbazyl). It seemed highly probable that one of the three compounds of Perkin and Tucker (*loc. cit.*) should have

this structure. Accordingly, each was reduced with hydriodic acid, in order that some clue to its constitution might be obtained. Dicarbazyl A (m. p. 220°) gave only carbazole. Dicarbazyl B (m. p. 265°) gave a substance which we have not yet identified, while the amorphous product C (m. p. 175°) gave carbazole and a high-melting, unknown compound. Since 9 : 9′-dicarbazyl on reduction should give only carbazole, dicarbazyl A seemed the most likely to have this structure. This assumption was readily verified by the direct bromination of dicarbazyl A, 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl (II) being obtained.

The foregoing experiments were repeated, 3 : 6-di-iodocarbazole being used, and dicarbazyl A iodinated.

All attempts to synthesise 9 : 9′-dicarbazyl have met with failure.

It has been shown (Wieland and Gambarjan, *loc. cit.*) that tetraphenylhydrazine may be converted into *NN′*-diphenylbenzidine by the action of cold concentrated sulphuric acid. The analogous conversion of 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl (Tucker, J., 1926, 3033) could not be brought about. *NN′*-Diphenylbenzidine is also obtained by oxidising diphenylamine in acid solution (Wieland, *Ber.*, 1913, **46**, 3296). This method of oxidation was applied to the 3 : 6-dihalogenocarbazoles in the hope that, since the 3 : 3′-compound could not be formed, a 1 : 1′-derivative might result. Only the 9 : 9′-dicarbazyl derivative was obtained, however, when acetic acid and sodium dichromate were used, whilst if sulphuric acid was present in the oxidising solution, a high-melting, amorphous substance was produced.

Attempts were made to oxidise 1 : 3 : 6 : 8-tetrabromocarbazole, by methods similar to those already described, with a view to obtain 1 : 3 : 6 : 8 : 1′ : 3′ : 6′ : 8′-octabromo-9 : 9′-dicarbazyl. The yield of the oxidation product was very small, however, and it is thought that the bromine atoms in the 1- and 8-positions must exercise some steric effect on the imino-group. This idea is substantiated by the fact that 1 : 3 : 6 : 8-tetrabromocarbazole could not be acetylated by the usual methods, nor could a nitroso-derivative be obtained.

The results obtained in the reduction of the amorphous substance C (Perkin and Tucker, *loc. cit.*) prompted some investigation into the structure of this compound, but so far the results have not justified us in assigning any formula to the substance.

EXPERIMENTAL.

3 : 6-*Dibromocarbazole.*—Some difficulty was experienced in obtaining this compound in quantity. The methods of List (Uerd. a. Rh. D.R.-P. 275,833) and of Mazzara and Leonardi (*Gazzetta*,

1895, **25**, ii, 397) were not suitable. A modification of Mazzara and Leonardi's method (*ibid.*, 1892, **22**, 569) was found to work fairly well, however.

(1) To a solution of 9-benzoylcarbazole (Stevens and Tucker, J., 1923, **123**, 2146; Tucker, *ibid.*, 1926, 546, footnote) (10 g.) in cold glacial acetic acid (140 c.c.), bromine (6 c.c.), dissolved in glacial acetic acid (10 c.c.), was added fairly rapidly. The product, which crystallised almost immediately, was removed after 3—4 hours, washed with a few c.c. of dilute alcohol, and crystallised twice from glacial acetic acid and once from benzene; 3 : 6-dibromo-9-benzoylcarbazole was then obtained in long, white needles, m. p. 213—214° (Found: Br, 37·9. Calc.: Br, 38·2%). The benzoyl derivative (2 g.) was hydrolysed by boiling it for ¼ hour with 5 c.c. of moderately concentrated alcoholic potash; short, white needles (from alcohol) of 3 : 6-dibromocarbazole, m. p. 211—213°, were obtained.

(2) A better method (similar to one described by Lindeman, *Ber.*, 1925, **58**, 2371), which we latterly used exclusively, was to brominate carbazole in carbon disulphide. Carbazole (50 g.) was dissolved in boiling carbon disulphide (600 c.c.), and a solution of bromine (34 c.c.) in carbon disulphide (130 c.c.) was added cautiously. The precipitated product was washed twice with cold carbon disulphide and crystallised twice from absolute alcohol; 3 : 6-dibromocarbazole, m. p. 211—213°, was then obtained (yield, 60%).

Oxidation of 3 : 6-*Dibromocarbazole.*—(1) *With potassium permanganate in acetone.** 3 : 6-Dibromocarbazole (5 g.) was dissolved in pure acetone (40 c.c.), finely powdered potassium permanganate (7 g.) added, and the solution boiled for 2—3 hours on the water-bath. The mixture was then poured into water, and sulphur dioxide passed through the suspension until there remained only a light reddish-brown solid, which was separated and extracted with boiling alcohol. The brown, alcohol-insoluble residue was crystallised twice from benzene, giving small, white cubes of 3 : 6 : 3′ : 6′-*tetrabromo*-9 : 9′-*dicarbazyl*, m. p. 249—250° (Found: Br, 49·2; *M*, cryoscopic in benzene, 629. $C_{24}H_{12}N_2Br_4$ requires Br, 49·4%; *M*, 648). This compound is very slightly soluble in alcohol, fairly easily soluble in acetone or glacial acetic acid, and very soluble in benzene, toluene, or xylene.

(2) *With sodium dichromate in acetic acid.* 3 : 6-Dibromocarbazole (2 g.) was dissolved in glacial acetic acid (40 c.c.), and sodium

* The acetone used in the oxidations described was purified by boiling it (2 l.) with powdered potassium permanganate (20—30 g.) for 1 hour. The acetone was recovered by distillation through a long column, the fraction, b. p. 55—57°, being retained for use.

dichromate (0·4 g.), dissolved in water (0·5 c.c.), was added. The green solution was boiled for ½ hour and poured into cold water, and the pink precipitate so produced was removed, thoroughly extracted with boiling alcohol (three times with 20 c.c.), and then crystallised twice from benzene. Small, white cubes of 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl, m. p. 249—250°, were obtained.

(3) *With sodium dichromate in acetic acid in presence of sulphuric acid* (compare Wieland, *loc. cit.*). An uncrystallisable brown solid, m. p. above 300°, was obtained.

Reduction of 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl.*—This compound proved exceedingly stable towards reducing agents and also towards reagents known to bring about the dissociation of tetraarylhydrazines. Boiling with zinc and glacial acetic acid (compare Wieland and Gambarjan, *loc. cit.*), or with the same reagents along with hydrochloric acid (Wieland and Haas, *Ber.*, 1922, **55**, 1804), or with tin and alcoholic–hydrochloric acid failed to effect any reduction. Similarly, the action of metallic sodium in an alcohol–benzene or in amyl-alcoholic solution produced no change.

No dissociation could be effected (*a*) by boiling with 2*N*-sulphuric acid (compare Franzen and Zimmerman, *Ber.*, 1906, **39**, 2566), (*b*) by treating an acetic acid solution with concentrated sulphuric acid, (*c*) by boiling in xylene for 1 hour (compare Wieland, *Annalen*, 1911, **381**, 200; 1912, **392**, 156), (*d*) by passing nitric oxide into a toluene solution of the dicarbazyl derivative at 90° (compare Wieland, *loc. cit.*).

Reduction with hydriodic acid. 3 : 6 : 3′ : 6′-Tetrabromo-9 : 9′-dicarbazyl (0·5 g.) was heated at 150° with concentrated hydriodic acid (3 c.c.) for 5 hours. The reaction mixture was then washed into a solution of sulphur dioxide in water. The white product thus obtained was well washed with water and extracted with boiling absolute alcohol, and the alcoholic extract was treated with animal charcoal and evaporated to dryness. The residue crystallised from benzene in white plates, m. p. 235—239°, identical with carbazole. That part of the reduction products which was insoluble in alcohol (0·03 g.) was shown, after recrystallisation from acetone, to be unchanged 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl.

Synthesis of 3 : 6 : 3′ : 6′-*Tetrabromo*-9 : 9′-*dicarbazyl.*—3 : 6-Dibromocarbazole (1 g.) and finely divided potassium (0·5 g.) were boiled together in pure, dry benzene (25 c.c.) for 1 hour. A yellow powder separated which was possibly the potassium derivative. The mixture was cooled, and iodine (0·6 g.) in dry benzene (10 c.c.) added. After ½ hour, the liquid was filtered, the residue washed with benzene containing a little iodine, and the combined filtrate and washings were evaporated almost to dryness; alcohol was then

added. The precipitated solid was extracted three times with boiling alcohol, and the insoluble portion crystallised first from benzene and then from glacial acetic acid, giving white plates, m. p. 249—250°, which were identical with the oxidation product of 3 : 6-dibromocarbazole. Yield 20%. No other products were isolated.

3 : 6-*Di-iodocarbazole* was obtained by Tucker's method (J., 1926, 546). A useful method of purification, which avoids preparation and subsequent hydrolysis of 3 : 6-di-iodo-9-acetylcarbazole, is as follows.

Crude 3 : 6-di-iodocarbazole (1 g.) was dissolved in acetone (20 c.c.), finely powdered potassium permanganate (0·15 g.) added, and the solution boiled for 20 minutes; it was then poured into a solution of sulphur dioxide. The white precipitate, on crystallisation from benzene, gave pure 3 : 6-di-iodocarbazole, m. p. 204—206°. The m. p. of the crude material may thus be raised about 15°.

Oxidation of 3 : 6-*Di-iodocarbazole.*—(1) *With potassium permanganate in acetone.* To a boiling solution of 3 : 6-di-iodocarbazole (2 g.) in a mixture of pure acetone (20 c.c.) and benzene (6 c.c.), a large excess (2—3 g.) of powdered potassium permanganate was added, in 4 portions, during 2 hours. The manganese precipitate was removed and extracted with benzene, the extracts were added to the main filtrate, and the whole was evaporated to dryness. The residue, after being washed with cold acetone, was crystallised from benzene–acetone; small, white cubes of 3 : 6 : 3′ : 6′-*tetraiodo*-9 : 9′-*dicarbazyl*, m. p. 269—270°, were then obtained (Found: I, 60·9; *M*, cryoscopic in benzene, 824. $C_{24}H_{12}N_2I_4$ requires I, 60·8%; *M*, 834). Yield 20%. Much unchanged 3 : 6-di-iodocarbazole was recovered from the acetone washings. 3 : 6 : 3′ : 6′-Tetraiodo-9 : 9′-dicarbazyl closely resembles the tetrabromo-compound. The crystalline form is the same, and the solubilities differ only in being slightly lower for the former.

In the above oxidation, the use of the mixed solvent (acetone–benzene) materially improved the yield of the oxidation product, which was rarely as much as 15% if acetone alone was used (compare Branch and Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 2411).

(2) *With sodium dichromate in glacial acetic acid.* 3 : 6-Di-iodocarbazole (1 g.) was dissolved in glacial acetic acid (80 c.c.), and sodium dichromate (0·5 g.), dissolved in the minimum quantity of water, was added. The solution was boiled for ½ hour. The flocculent precipitate was removed and extracted with alcohol, and the insoluble portion was crystallised, first from benzene–acetone and then from benzene; small, white cubes, m. p. 269—270°, of 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl were thus obtained.

Synthesis of 3 : 6 : 3′ : 6′-*Tetraiodo*-9 : 9′-*dicarbazyl*.—3 : 6-Di-iodocarbazole (1 g.) was added to finely divided potassium (0·3 g.) in pure dry benzene (20 c.c.), and the mixture boiled for 1½ hours. As in the case of 3 : 6-dibromocarbazole, a yellow solid separated. After the mixture had cooled, a solution of iodine (0·5 g.) in dry benzene (10 c.c.) was added with constant shaking. After 1 hour, the liquid was filtered, the residue washed with benzene containing iodine, and the combined filtrate and washings were evaporated to dryness. The solid thus obtained was extracted with alcohol (to remove unchanged 3 : 6-di-iodocarbazole), and the insoluble residue crystallised from benzene (animal charcoal), white cubes, m. p. 269—270°, identical with the oxidation product of 3 : 6-di-iodocarbazole, being deposited.

Reduction of Dicarbazyl A (m. p. 220°).—Dicarbazyl A (0·5 g.) was heated under pressure with concentrated hydriodic acid at 150° for 15 hours. The reaction mixture was washed into water, and the suspension treated with sulphur dioxide to remove free iodine. The separated solid was completely soluble in boiling alcohol, indicating that no dicarbazyl A remained unreduced, since this substance is insoluble in alcohol. The alcoholic solution deposited yellowish needles, which, after one crystallisation from benzene, melted at 235—238° (with sublimation) and were identified with carbazole in the usual way. No other substance could be detected.

Reduction of Dicarbazyl B (m. p. 265°).—The treatment of dicarbazyl B (0·2 g.) with hydriodic acid (3 c.c.) was that described for dicarbazyl A. The product was soluble in alcohol and was a white, non-crystallisable substance, m. p. 100—110°, which has not yet been identified, but is being further investigated.

Reduction of the Amorphous Product C (m. p. 175°).—The substance C (0·5 g.) was heated with concentrated hydriodic acid for 20 hours at 150°. The product of reduction was isolated as in the reduction of dicarbazyls A and B. The major portion of it was soluble in alcohol; the solution deposited small plates, m. p. 235—238°, identical with carbazole. The alcohol-insoluble portion, after repeated extraction with the solvent, melted at 245—260°. It was dissolved in benzene and the solution, after being boiled with animal charcoal for ¼ hour, was filtered into excess of boiling alcohol. The precipitated solid was redissolved in benzene and the foregoing process repeated five or six times; there was then obtained a small amount of a cream-coloured, amorphous substance, m. p. 300—310°, which would not crystallise from any solvent. It is being further investigated.

Bromination of Dicarbazyl A.—It was found essential to use very pure dicarbazyl both in bromination and in iodination. Even an

amount of impurity causing a depression of 2—3° in the m. p. of dicarbazyl A makes it almost impossible to purify the product of halogenation.

Dicarbazyl A (0·5 g.) was dissolved in the minimum quantity of boiling glacial acetic acid, a solution (3·5 c.c.) of bromine (1 c.c.) in glacial acetic acid (9 c.c.) gradually added, and the turbid mixture heated on the water-bath for ½ hour; small, white, glistening plates had then separated. After cooling, these were removed, washed with boiling alcohol, and crystallised twice from benzene, small, hard cubes, m. p. 249—250°, identical with synthetic 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl, being obtained.

Iodination of Dicarbazyl A.—(1) To a solution of pure dicarbazyl A (0·5 g.) and finely divided iodine (0·75 g.) in boiling glacial acetic acid (35 c.c.), concentrated nitric acid (2·5 c.c.) in glacial acetic acid (10 c.c.) was added drop by drop until the iodine colour was discharged. After cooling, the precipitated product was removed and washed with sulphur dioxide solution and boiling alcohol. The residue crystallised from benzene in slightly yellow cubes, m. p. 269—270°, and was identical with synthetic 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl. The yellow colour, which was probably due to slight nitration, was not removed by animal charcoal.

(2) To a solution of dicarbazyl A (0·23 g.) in the minimum quantity of glacial acetic acid were successively added powdered potassium iodide (0·36 g.) and, after slight cooling, powdered potassium iodate (0·5 g.). The whole was boiled until the iodine colour had vanished, and was then poured into a solution of sulphur dioxide. The product was 3 : 6 : 3′ : 6′-tetraiodo-9 : 9′-dicarbazyl.

9 : 9′-*Dicarbazyl.*—We made several attempts to convert 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl, but without success. Solid 9 : 9′-dicarbazyl, or a solution in glacial acetic acid, was unaffected by cold, and sulphonated by hot, concentrated sulphuric acid. Hydrochloric acid or acetic anhydride, heated under pressure with 9 : 9′-dicarbazyl, produced no change.

Many fruitless attempts were also made to synthesise 9 : 9′-dicarbazyl (i) by removal of sulphur from di-*o*-thiotetraphenylhydrazine (Pesci, *Gazzetta*, 1916, **46**, i, 103; compare Goske, *Ber.*, 1887, **20**, 233), (ii) by the action of halogens on 9-potassiocarbazole. The action of finely divided potassium on carbazole did not give 9-potassiocarbazole as in the case of the halogen derivatives.

Oxidation of 1 : 3 : 6 : 8-*Tetrabromocarbazole.*—Potassium permanganate in acetone would not oxidise this compound.

1 : 3 : 6 : 8-Tetrabromocarbazole (Votoček, *Chem. Ztg.*, 1896, **20**, 190) (1 g.) was dissolved in boiling glacial acetic acid (60 c.c.), and sodium dichromate (0·75 g.) was added. After boiling for 1 hour,

the mixture was poured into water, and the precipitate was separated and extracted with warm acetone. The insoluble residue, after several crystallisations from benzene, gave a minute quantity of small crystals, m. p. above 300°, insoluble in acetone or alcohol and almost so in glacial acetic acid. A sufficient quantity for analysis has not yet been obtained.

Amorphous Substance C, m. p. 175° (Perkin and Tucker, *loc. cit.*). —Analysis of *C* gave C, 86·8; H, 5·1; N, 8·1; *M*, 546. $C_{36}H_{23}N_3$ requires C, 86·9; H, 4·6; N, 8·45%; *M*, 497. Distillation from a paraffin bath at 300° produced carbazole and a residue, which, after purification in a manner similar to that used for the high-melting reduction product of C, was obtained as a cream-coloured solid, m. p. about 320° (Found: C, 86·1, 86·2; H, 4·9, 4·95; N, 8·2, 8·0. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·9; N, 8·4%). No crystalline derivative of this could be obtained, nor any acetyl, methyl or halogen derivative of the amorphous substance C.

The substance C was not produced by prolonged treatment of 9 : 9′-dicarbazyl with potassium permanganate in acetone.

Summary.

(*a*) 3 : 6 : 3′ : 6′-Tetrabromo-9 : 9′-dicarbazyl (m. p. 249—250°) has been prepared by the oxidation of 3 : 6-dibromocarbazole and has been synthesised by the action of iodine on 3 : 6-dibromo-9-potassiocarbazole.

3 : 6 : 3′ : 6′-Tetraiodo-9 : 9′-dicarbazyl has similarly been prepared and synthesised.

(*b*) The dicarbazyl A, m. p. 220°, of Perkin and Tucker (*loc. cit.*), on bromination, gave 3 : 6 : 3′ : 6′-tetrabromo-9 : 9′-dicarbazyl. It is therefore concluded that dicarbazyl A is 9 : 9′-dicarbazyl.

(*c*) It has not been found possible to convert 9 : 9′-dicarbazyl into 3 : 3′-dicarbazyl.

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